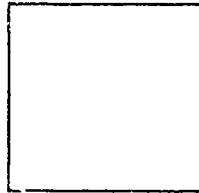


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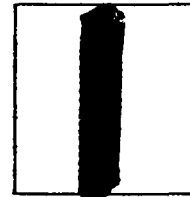
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AN INVESTIGATION TO DETERMINE THE POSITION ON THE
ELECTROMOTIVE SERIES OF TINLESS SOLDERS
AND
THEIR RELATION TO CORROSION

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1928

Submitted in Partial Fulfillment of the Requirement
for the Degree of
Master of Science

From the

Massachusetts Institute of Technology

1934

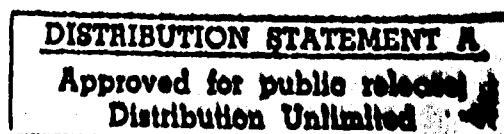
Signature of Author _____

Department of Mechanical Engineering, May 18, 1934

Professor in Charge of Research _____

Chairman of Departmental }

Committee on Graduate Students) _____



ACKNOWLEDGEMENT

The author wishes to express his appreciation for the advice and assistance of Dr. P. R. Kosting, Watertown Arsenal, whose aid and counsel were invaluable in the conduct of this investigation.

The use of the facilities of Watertown Arsenal was obtained through the kindness and cooperation of the Commanding Officer, Colonel G. F. Jenks, Ordnance Department.

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CONCLUSIONS (Abstract)

1. The presence of tin in a solder for use on copper has a very corrosive effect, increasing with an increase in the acidity of the electrolyte.
2. A tinless solder of composition Pb 78.8 - Cd 19.7 - Zn 1.5 is far superior in every respect for use on copper and removes all harmful effects of tin.
3. The presence of tin (even in very small proportions) in a solder for use on iron fosters corrosion in weakly acidic solutions. In a strongly acidic solution its corrosive effect lasts only for a brief period at the start. In the latter case the iron is protected but the anode, (alloy formed on application of solder), corrodes rapidly.
4. A tinless solder of composition (Pb 78.8 - Cd 19.7 - Zn 1.5) is superior in every respect for use on iron than one containing tin.
5. The presence of tin in the coating of Terne plate removes all advantages to be gained by use of tinless solder.
6. There is no definite correlation between the equilibrium potentials of solders and their possible corrosive effects. This is to be expected as in a soldered joint the alloy formed is the corrosive influence and not the pure solder.

INTRODUCTION

1

General

The failure of soldered joints due to an excessive and accelerated corrosion of the parent metal at its juncture with the solder has made imperative an investigation into its causes, and if possible the development of preventative measures. The use of the present standard 50-50 solder (Pb-Sn) is practically universal, notwithstanding the fact that the corrosive effect of tin and tin compounds upon many metals is common knowledge throughout the interested industries. Its effect is especially marked upon copper and iron when exposed to simple galvanic action. The corrosion of cartridge containers at the soldered joints, and the shearing off of the inertia pellets on the spiral springs of Mark I long fuzes caused by deep line-type corrosion, are excellent examples of its action when used upon low carbon steels.

Thus it is found that the leading investigators in this field have turned to tinless solders as the solution to their problem. Alloys consisting of lead, cadmium, zinc, and bismuth have shown promise of overcoming this corrosive effect and lately there has been considerable activity in the endeavor to determine the best composition.

Specific

2

It is the object of the writer to: (1) Conduct a detailed investigation of one solder of the following composition Pb 78.8% - Cd 19.7% - Zn 1.5 to determine its reliability for use upon iron and copper. (2) To determine the position on the electromotive series of tinless solders and their relation to corrosion.

This particular solder was chosen because in a parallel investigation by Mr. H. G. Carter, Watertown Arsenal, upon the comparative physical properties of some forty-five (45) tinless solders, this one was found to exhibit the best properties of all those tried, and to be superior in that respect to 50-50 (Pb-Sn) solder.

HISTORY

3.

Before entering into a discussion of the historical background of this subject it would be well to define a few terms used by the electro-chemist so as to avoid any misconception of the following statements:

The engineer is interested in the flow of electricity outside of the cell and consequently considers the positive pole as the source from which current flows. Actually the current flows from the negative pole or electrode into the electrolyte, thence to the positive pole and out. Inasmuch as the electro-chemist is interested only in what happens within the cell, he is especially interested in this negative pole where usually metallic atoms become ions and migrate to the positive pole. This is the pole that is going to be corroded due to the transformation of atoms to the ionic state and subsequent migration. He calls this the anode. Thus to say that a particular metal or compound is anodic to another is to imply that the former will suffer the more extreme corrosion. Of course the reverse would be true if it were cathodic. This terminology will be used throughout.

The problem of corrosion has undoubtedly been with us since the earliest times, but active investigation into its causes and prevention is a product of comparatively recent years. Probably one of the most significant facts pertaining to corrosion--that a neutral water tends to become alkaline during the

process of corrosion was not discovered until 1788 by the chemist Austin. Thus it is apparent that the increased use of metals, especially of steel as a substitute for the non-ferrous alloys, has focussed our attention upon the necessity of devising preventive measures to overcome the serious losses suffered by industry of the present day.

The history of corrosion is essentially an exposition of the different theories which have been advanced as to its causes. However, in the specific question in hand the only cause necessary to consider is that due to galvanic action.

In this field, and even further narrowing it down to a consideration of the work done upon tinless solders, and the effect of our common 50-50 (Pb-Sn) solder on iron and tin there are a few outstanding leaders.

The work of Paul D. Merica of the Bureau of Standards upon the corrosive effects of tin upon copper has been universally accepted. In his investigation he dealt with tinned sheet copper, experimental samples of which he received from tinned sheet copper roofing actually in use at the time. Amongst others he had samples from the roofing of the Library of Congress and the State House of Texas. To reproduce these conditions in the laboratory and to give a clearer indication of the effect and existence of alloy formation, he prepared laboratory samples by heat treating

electrolytic copper coated with Banca tin. He found the presence of two alloys and the eutectic in his homogenized samples. He then set up electrolytic cells composed of these specimens and the pure copper strip, using varying electrolytes. In all cases he found the eutectic to be anodic to copper and therefore tending to reduce corrosion. However, the eutectic is merely a mechanical protection and as soon as this protective barrier was broken down by scratching or due to natural corrosion the copper began to fail rapidly. It must be noted that in the use of electrolytes his solutions were essentially acidic. The two underlying alloys were found to be cathodic to copper and thus foster corrosion. His investigation showed that the tin coating on copper consisted of two distinct alloy layers next to the copper and finally a layer of the eutectic, that the alloy layers are cathodic to both the outer tin eutectic and the underlying copper, and less readily attacked by water and dilute acids (also alkalies). As long as there was any presence of the tin eutectic the metal was protected, but any failure in this outer layer produced rapid pitting. In his laboratory homogenized specimens he attempted to simulate this effect by dissolving the eutectic by boiling in concentrated HCl for a few minutes. He found that when done properly, the copper corroded (or was anodic) but that if there was any tin present (not completely

removed by the boiling) the copper was protected (cathodic). This investigation is of fundamental importance as it forms a basis for comparative effects in the field of tinless solders, inasmuch as a similar effect should be apparent in the alloying of a tin solder with copper.

In the investigation of the use of tinless solders upon copper there has been some very recent work done by Mr. Howard Sheaff of the research laboratories of the National Lead Company. His investigation has confined itself mainly to combinations of Lead-Cadmium Zinc and Bismuth solders with which he has had some success. He seems to find the best solder to be one of Lead 35.4 - Cadmium 14.23 - Zinc 0.23. He also states that the proportions of zinc should never exceed 1%.

There has been considerable work done along similar lines by the Bureau of Standards and the Copper and Brass Research Association of New York but essentially it has been a verification of Merica's work and more detailed studies of the effect of tinless solders upon different metals. This latter field is still in its infancy and expanding rapidly.

Theory Pertaining to This Investigation

Galvanic corrosion may be defined as rapid corrosion of a metal due to its being in electrical contact with another metal in the same electrolyte and subject to corrosive conditions. It is caused

by the difference between the individual tendencies of metals to be acted upon or combine with corrosive materials. With proper apparatus this difference in tendency of two metals to corrode can be measured in volts. This is the voltage of the galvanic cell and is the driving force behind galvanic corrosion. The main characteristic of this type of corrosion is that one metal suffers extensive corrosion while the metal adjacent to it does not suffer to such an extent. There has been published some useful data on galvanic corrosion and the following galvanic electromotive series has been advanced:

Corroded End (Anodic)

{ Magnesium
{ Aluminum

{ Zinc
{ Cadmium

{ Steel
{ Iron
{ Chromium Iron (active)
{ Chromium - Nickel - Iron (active)

{ Solder 50-50 (Pb Sn)
{ Tin
{ Lead

{ Nickel
{ Brasses
{ Bronzes
{ Monel
{ Copper

{ High 18% chrome stainless alloy (passive)
{ Chromium Nickel Iron (passive)

Silver Solder

{ Silver
{ Gold
{ Platinum

Protected end (cathodic)

8

Connecting two metals in different groups on the list results in the more anodic metal being corroded if dipped in dilute water solutions of salts, acids or alkalis. Metals grouped together in one group usually have no tendency to cause galvanic corrosion.

However, it must be realized at this point that the short circuited cell set up in a soldered joint is not composed of the metal and the pure solder. We are dealing with the alloy formed in the soldering process so this table is of interest only in showing that although, for instance, 50-50 solder is anodic to copper the alloy formed in a soldered joint of copper and 50-50 solder is cathodic.

This series shows the tendency to corrode, but actual galvanic corrosion takes place only when current flows. To allow current to flow certain conditions are necessary:

- 1) There must be good conductivity, that is, good electrical contact must be maintained between both metals through the electrolyte.

- 2) There must be good contact surfaces, because often formation of gases on the protected surface, (Hydrogen especially) and also insoluble protective films on either the protected (cathodic) or corroded (anodic) surface materially impedes the progress of corrosion.

3) The surfaces must be close together.

4) A large unprotected (cathodic) area fosters rapid corrosion as do small anodes.

5) High Electro-Motive Forces aid the progress of corrosion.

It is evident that to place one's finger upon the specific reason for the corrosive or non-corrosive effect of different galvanic couples would require a very careful study. However, the measure of the resultant effect of all the above factors is the flow of current. The potential is the tendency to corrode--the intensity factor--but of far more importance is the extent of corrosion, which depends upon the quantity of electricity that flows, the current or the capacity factor. It is intended in the performance of this investigation to deal with current densities alone and by running a comparative test with 50-50 (Pb-Sn) solder and the new tinless solder of composition Pb-78-8-Cd 19.7 - Zn 1.5 to determine their relative value for use on copper and iron.

The electromotive series is very useful in predicting the magnitude of the Electro Motive Forces set up and the anode and cathode of any combination of metals in an electrolyte. However, it must be remembered that industry deals very considerably with alloys rather than pure metals. In the case of an alloy which consists of two or more phases the equilibrium potential

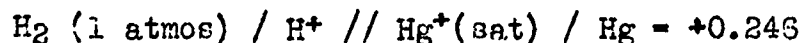
is usually that of the more reactive or baser phase present. If the two or more metals in the alloy are mutually soluble the equilibrium potential increases continually with an increase in the composition of the nobler metal. If a metallic compound is formed, unsoluble in either metal, the equilibrium potential of the compound is in between that of the base and noble alloy. The potential of any composition can, therefore, be estimated if the equilibrium potentials of the two constituents are known as well as the equilibrium diagram. The above statements are taken from a publication entitled "Corrosion Theory" by Dr. P. R. Hosking of Watertown Arsenal. It is well to bear in mind that these general rules are truly general in nature and cover only the usual case. There are many exceptions too numerous to mention. The nature of the electrolyte affects the potential very materially; often an alloy or metallic compound which seems to prove the rule in one solution will completely disprove it in another. When you consider the innumerable number of alloys and metallic compounds and the equally large number of electrolytes that might be chosen it is obvious that this field has hardly been touched and that theories must be reserved for more complete data. Also, another factor of major importance, is that some metals do not seem capable of reaching an equilibrium potential in certain electrolytes. The reason for this is still being studied and at the present time no satisfactory

conclusion has been reached. In such cases a close approximation may be hazarded by arriving at an average value where the curve of potential against time begins to become asymptotic to some potential value. This is the best that can be done in such cases and applies to the particular study in hand. Further mention of this fact will be made in the "Discussion of Results".

Before leaving this subject there are certain conventions regarding signs which must be mentioned.

1) Outside the cell positive electricity flows toward the negative pole; inside the cell positive electricity flows from the negative pole.

2) The potential of a single electrode half cell is determined by reference to the N hydrogen electrode, which is placed at the left for reference and combined with the electrode in question at the right. As this investigation will be conducted using a saturated calomel half cell, the following is an example of the manner in which the flow would be written:



$\xrightarrow{\hspace{1.5cm}}$
 direction of + electricity
 within the cell

Thus using an electrode whose potential is to be determined the flow is written in the order, Electrolyte / Electrode, and a positive value means that + electricity flows from left to right, from solution to

electrode. To illustrate: The case of 50-50 (Pb-Sn) solder in this investigation would be written as follows: (Using saturated calomel half cell and Sea Water electrolyte)

Hg / Hg⁺ (sat) // Sea Water / 50-50 Solder

—————→ reading +
direction of + electricity

←———— reading -

The sign of an electrode gives the sign of the charge of the electrode against the solution when connected to the normal H₂ electrode. Noble metals are + and base metals - .

The writer intends to use the saturated calomel half cell whose value is + 0.246 volts to determine the equilibrium potential of copper, iron, 50-50 (Pb-Sn) solder, and two tinless solders (composition given in description of experiment) using synthetic Sea Water as an electrolyte and to determine any relation between these values and their effect on corrosion as set forth in the first part of this study.

1) Preparation of Specimens:

The following specimens were prepared; all three inches long by one inch wide:

	<u>No. of Specimens</u>
50-50 (Pb-Sn) solder	(3)
Pb 78.8 - Cd 19.7 - Zn 1.5 solder	(3)
Copper + 50-50 solder heat treated	(2)
Copper + Cadmium solder heat treated	(2)
Electrolytic copper strips	(5)
Bright annealed low carbon steel	(5)
Steel (as above) + 50-50 solder	(2)
Steel (as above) + Cadmium solder	(2)
Pb 80.7 - Cd 17.3 - Bi 2 solder	(1)

The copper strips were of electrolytic copper and were carefully cleaned and sand-papered before use.

The steel used (hereafter referred to as iron) was a low carbon bright annealed steel such as used in cartridge containers, .013 in. thick.

The heat treated specimens were prepared by carefully removing any film coating, fluxing with $ZnCl_2$, and dipping several times in a molten solder bath to insure a good even coating. These specimens were then heat treated at 500°C for five hours, each specimen surrounded with powdered charcoal to prevent oxidation. They were then cleaned by removing any clinging carbon particles with fine emery paper until

a clean surface was obtained. A sample was then cut off the bottom of each specimen for micro-etching. These samples were then electroplated with copper, mounted, polished, etched, and a micro-photograph taken.

The solder specimens were weighed out according to specifications and melted in a porcelain crucible in an oxygen free (approximately) atmosphere to prevent the formation of excessive dross. This was accomplished by heating the crucible in a larger silicon crucible the latter having a cover through the center of which a gas flame was played, thus using up most of the available oxygen. The molten solder was then poured into an aluminum mold of dimensions 3" x 1" x 1/8". When ready for use these specimens were brazed with a knife to remove any film.

2) Apparatus

The potentiometer was manufactured by Leeds and Northrup and was calibrated by use of a standard Weston Cell before each set of readings at which there had been any appreciable length of time since the last readings, at least once daily. The battery used with the potentiometer was an Exide battery. The galvanometer was of the suspended mirror type. It was firmly attached to the wall to reduce the possibility of any vibrational effect. A special instrument was used in the coupling to the galvanic cells.

When the vertical switches (see photograph figure 2) are up the cells are shorted. The switch is pressed down to close the circuit.

All ingredients for use in the calomel half cell were certified chemically pure. A better idea of the set-up will be obtained by the close-up photograph, Fig. 1. A photograph of the entire set-up is given on Fig. 2. A diagrammatic sketch of the electrical connections is shown on Fig. 3.

3) Method of Procedure

The milli ammeter was first calibrated by the use of a standard 10 ohms resistance and the potentiometer. The following galvanic cells were then prepared by separating the two specimens by a round hard rubber insulator one inch in diameter. One square inch of each specimen was exposed, the rest being covered with paraffin.

Copper vs 50-50 solder

Copper vs Cadmium solder

Copper vs heat treated copper + Cadmium solder

Iron vs 50-50 solder

Iron vs Cadmium solder

Iron vs heat treated iron + 50-50 solder

Iron vs heat " " " Cadmium solder

Iron vs heat treated Terne coat + Cadmium solder

It might be well at this point to explain the latter cell. Terne coat is a low carbon steel (usually) covered with a fine lead-tin coating, this particular

specimen was .018 inches thick.

It was decided to use Sea Water as an electrolyte because much of the corrosion reported, especially in the case of the iron had taken place close to the seaboard in a damp atmosphere and these conditions could best be approximated in this way. The P_H of this electrolyte was obtained by the dye color method. It was found to be 6.25 (slightly acidic).

Two hundred and fifty c.c. (250 c.c.) beakers were used to hold the specimens, each having been rinsed in distilled water. One hundred and twenty-five c.c.'s (125 c.c.) of Sea Water was added to the empty beakers (each). The switch corresponding to the particular cell was depressed (thus forming a closed circuit) and the cell immersed in the solution. An instantaneous value of the current was read. Readings were taken every minute for five minutes, then every five minutes for an hour. Readings were then taken without any definite plan, attempting to take at least one a day until the cell appeared to be reaching a point of equilibrium when greater elapsed time was allowed. Notations were made throughout the test as to change in color of solution, formation of precipitates, and other pertinent data that might prove of interest. These cells were covered with a larger beaker to protect them from dust during the run.

These were allowed to run until an equilibrium point had been definitely reached. Then 5 c.c. of HCl was added to each beaker to determine the effect of a little stronger acidity, corresponding to a more acidic atmosphere as might be encountered close to a large seaport town where the fumes of factories materially (relative only) acidify the atmosphere. The procedure was then the same as for the previous run.

In the determination of the equilibrium potential the saturated calomel half cell was used with a KCl bridge. This is best diagrammatically shown in figure 1. The bridge was formed by an inverted U tube of 1/4" glass tubing with a vertical member fused into the center of the horizontal member of the U. In this way it was possible to draw the solution up into the vertical member and then by clamping the rubber nose extension to hold the liquid there. This method gave positive proof that the U tube was full as it was possible to hold the surface of the liquid in the bridge well up in the vertical member. The portions of the U immersed in the solution were drawn out with a right angle bend to about 1/16" in diameter. This aids in preventing diffusion of the KCl into the Sea Water in the last beaker. The specimen used was the same as used in the previous portion of this investigation and similarly prepared. As close to an instantaneous value as possible was obtained (about 10 sec) using the potentiometer and galvanometer set-up

to take readings. Readings were taken every five minutes until a condition of equilibrium was approached. As previously discussed these values never did reach a point of absolute equilibrium but in an electrolyte as chosen this was not expected. When differences between successive readings had diminished to the order of magnitude of a few thousandths the readings were discontinued. Much closer differences were obtained than this in several cases.

18 (a)

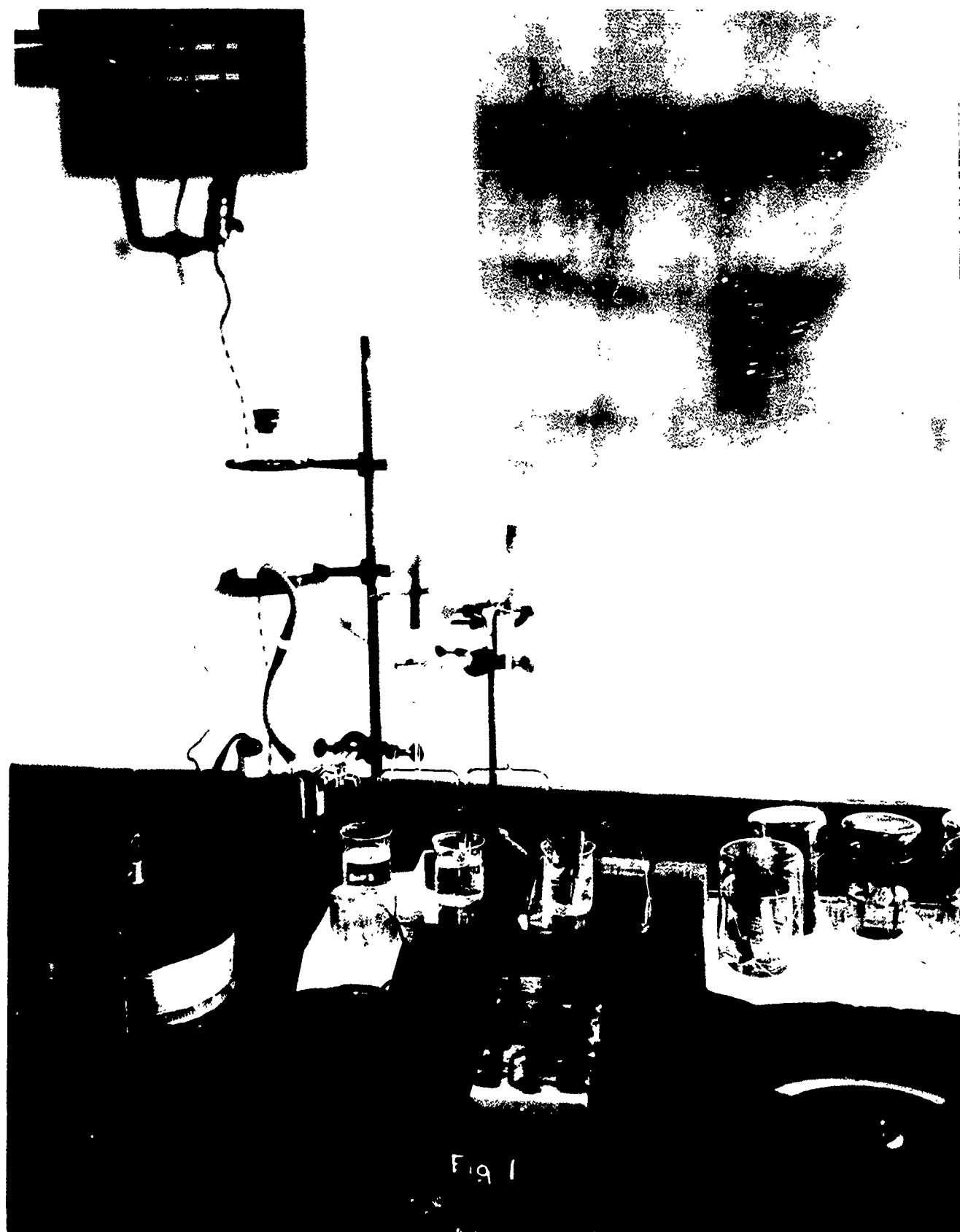
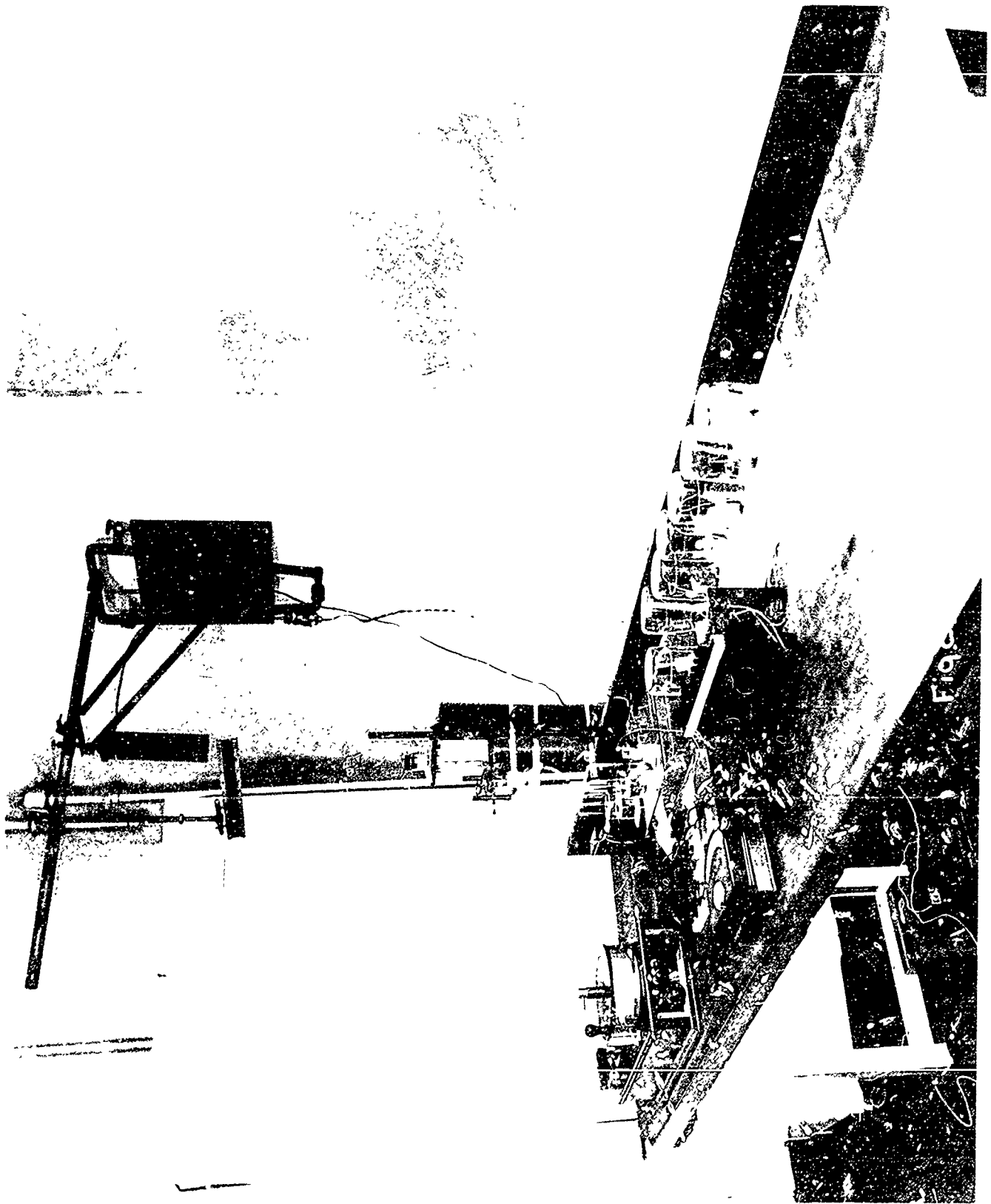
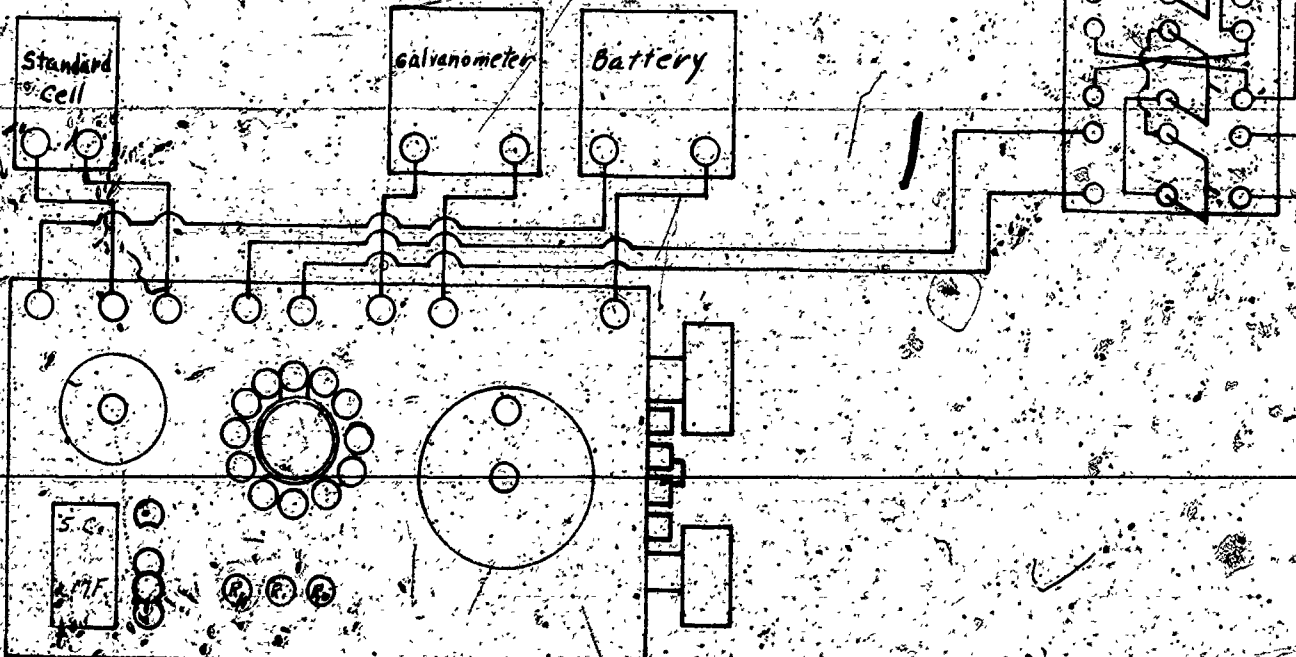
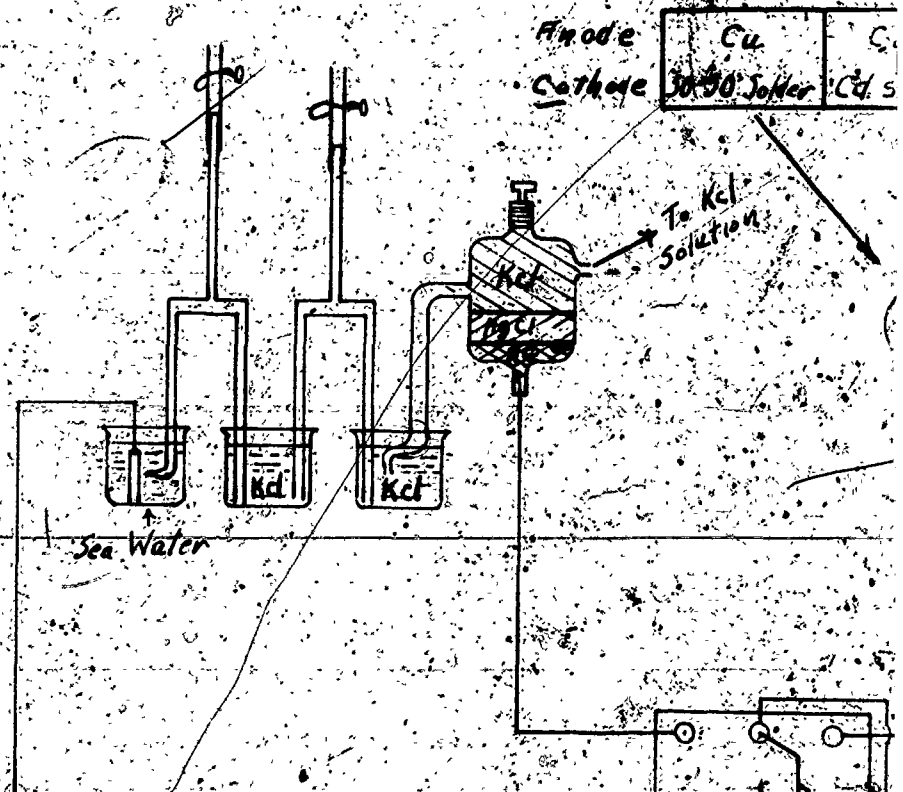
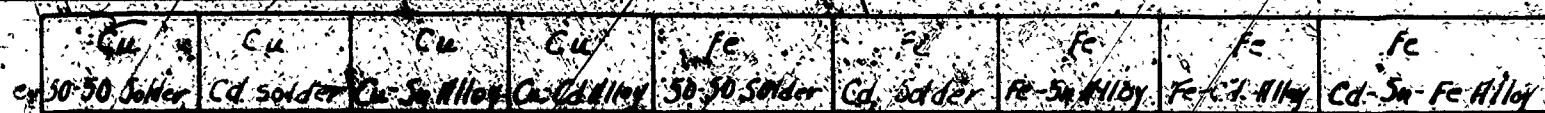


Fig 1

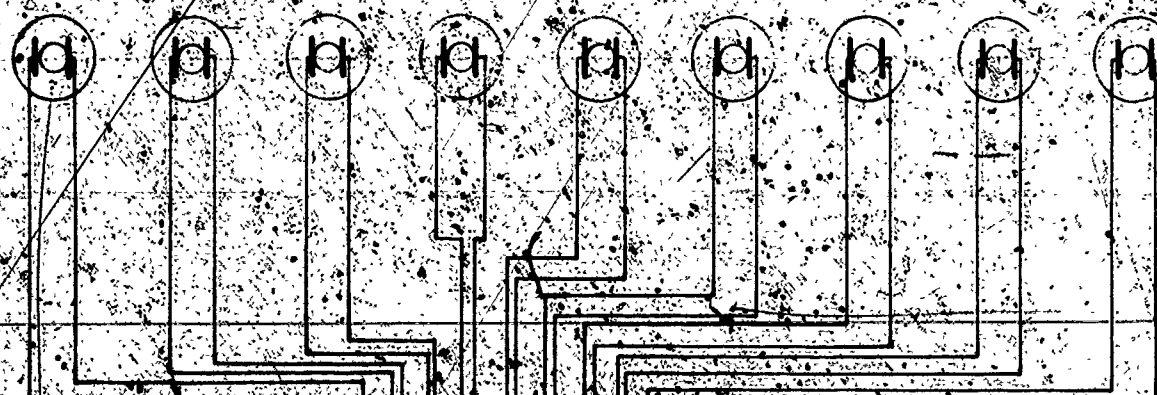


Figure





To KCl Solution



Cell Shorted - Switch pressed to open circuit

Copper
vs
50-50 (Pb-Sn) Solder
+ = Anode solder
- = Anode copper
Electrolyte - - Sea Water

<u>Time</u> <u>Minutes</u>	<u>Reading</u> <u>Milli - Amperes</u>
0	.586
1	.201
3	.147
10	.088
20	.061
30	.056
40	.058
50	.057
60	.056
Hours	
8	.047
25	.026
46	.028
78	.0233
125	.029
200	.029
Electrolyte --Sea Water -- 5% Hcl	
<u>Minutes</u>	
0	.142
60	.029
Hours	
5	.029
29	.029
49	.029
78	.029

Copper

20

vs

Cadmium Solder

+ = Anode solder

- = Anode copper

Electrolyte -- Sea Water

Time Minutes	Reading Milli - Amperes
0	1.65
1	.33
5	.17
10	.16
20	.11
30	.12
40	.13
50	.10
60	.09
Hours 3	.035
6	.047
21	.025
70	.05
101	.085
121	.120
149	.135
300	.120
Electrolyte -- Sea Water - 5% Hcl	
Minutes 0	.70
60	.41
Hours 2	.27
3	.28
22	.29
41	.23
200	.195
368	.160

Copper

21

vs

Copper + 50-50 (Pb-Sn) solder (heat treated)

+ = Anode heat treated specimen

- = Anode copper

Electrolyte - - Sea Water

Time Minutes	Reading Milli - Amperes
0	.146
30	.056
60	0
Hours	
2	-.102
5	-.059
10	-.023
15	-.015
30	-.010
40	-.006
60	-.006
Minutes	Electrolyte -- Sea Water - - 5% HCl
0	-1.02
10	-.117
60	-.044
Hours	
2	-.0293
4	-.0293
5	-.0293
24	-.0293
27	-.0293
28	-.0293
57	-.0293

Copper

22

vs

Copper + Cadmium Solder (heat treated)

+ = Anode heat treated specimen

- = Anode Copper

Electrolyte -- Sea Water

<u>Time</u> <u>Minutes</u>	<u>Reading</u> <u>Milli - Amperes</u>
0	.44
1	.17
5	.138
10	.094
20	.064
50	.0615
40	.0535
50	.0615
Hours	
4	.006
55	.003
79	.003
103	.006
122	.003
127	.0015
171	.000
195	.000
200	.000
Electrolyte -- Sea Water -- 5% Hcl	
Minutes	
0	.38
60	.054
Hours	
4	.064
7	.064
26	.061
45	.060
201	.006
370	.006

Iron

23

vs

50-50 (Pb-Sn) Solder

+ = Anode solder

- = Anode iron

Electrolyte -- Sea Water

<u>Time</u> <u>Minutes</u>	<u>Reading</u> <u>Milli - Amperes</u>
0	.12
1	0
5	0
10	-.015
15	-.023
20	-.026
30	-.026
40	-.023
50	-.026
60	-.026
Hours	
2	-.029
51	-.044
75	-.059
99	-.06
120	-.055
123	-.040
195	-.032
200	-.032

Electrolyte -- Sea Water -- 5% Hcl

<u>Minutes</u>	
0	.205
60	.38
Hours	
4	.54
6	.50
25	.22
44	.205
63	.205

Iron

24

vs

Cadmium Solder

+ = Anode solder

- = Anode Iron

Electrolyte - - Sea Water

<u>Time</u> <u>Minutes</u>	<u>Reading</u> <u>Milli - Amperes</u>
0	4.5+
1	.23
3	.14
5	.12
10	.11
20	.07
30	.062
40	.059
50	.056
60	.056
Hours	
2	.056
53	.03
77	.03
101	.03
125	.026
200	.023
Electrolyte - - Sea Water -- 5% Hcl	
Minutes	
0	4.5+
60	3.2
Hours	
4	2.3
7	2.2
30	2.05

vs

Iron † 50-50 (Pb-Sn)solder (heat treated)

† = Anode heat treated specimen

- = Anode Iron

Electrolyte -- Sea Water

<u>Time</u> <u>Minutes</u>	<u>Reading</u> <u>Milli - Amperes</u>
0	-.44
1	-.32
5	-.20
10	-.17
20	-.085
30	-.065
40	-.062
50	-.059
60	-.055
Hours	
52	-.044
76	-.050
100	-.050
124	-.044
172	-.035
196	-.035
Electrolyte -- Sea Water -- 5% Hcl	
Minutes	
0	-1.06
60	-.035
Hours	
4	.023
6	.044
25	.082
44	.150
63	.185
183	.134
400	.260

Iron
vs

26

Iron†Cadmium solder (heat treated)
† = Anode heat treated specimen
- = Anode Iron

Electrolyte -- Sea Water

<u>Time</u> <u>Minutes</u>	<u>Reading</u> <u>Milli - Amperes</u>
0	4.5
1	.47
5	.15
10	.06
Hours 20	.009
23	.009
42	-.003
50	-.003

Electrolyte -- Sea Water -- 5% Hcl

<u>Minutes</u>	
0	† off scale
1	3.3
10	2.0
60	.24
Hours 20	.17
200	.027

Iron

27

vs

Terne Plate † Cadmium solder (heat treated)

† = Anode heat treated specimen

- = Anode Iron

Electrolyte -- Sea Water

<u>Time</u> <u>Minutes</u>	<u>Reading</u> <u>Milli - Amperes</u>
0	-.12
1	-.14
5	-.108
10	-.094
20	-.08
30	-.062
40	-.062
50	-.062
60	-.059
Hours	
52	-.055
76	-.065
100	-.071
121	-.047
145	.035
169	.035
193	.032
Electrolyte -- Sea Water - 5% Hcl	
<u>Minutes</u>	
0	off scale
60	-.29
Hours	
4	-.059
6	-.059
25	-.015
44	.052
63	.059
183	.035
400	.029

Measurement of Equilibrium Potentials
Saturated Calomel Half Cell - Electrolyte Sea Water

50-50 (Pb-Sn) Solder

Time-Minutes	Reading-Volts	Difference
0	-.52750	--
5	-.51334	-.01416
10	-.50905	-.00429
15	-.50540	-.00365
20	-.50295	-.00245
25	-.50120	-.00175
221	-.49700	-.00420

Solder - (Pb 78.8 - Cd 19.7 - Zn 1.5)

0	-.75232	--
5	-.74514	-.00718
10	-.74181	-.00333
23	-.72722	-.01459
30	-.72076	-.00646
40	-.71470	-.00606
60	-.71000	-.00470

Solder - (Pb 80.7 - Cd 17.3 - Bi 2)

Time Minutes	Reading Volts	Difference
0	-.72477	--
5	-.71756	-.00721
10	-.71242	-.00514
15	-.71372	+.00130
20	-.71276	-.00096
25	-.71351	+.00075
60	-.71232	-.00119

Bright Annealed Low Carbon Steel

0	-.56873	--
5	-.59740	+.02867
10	-.60648	+.00908
15	-.61214	+.00566
20	-.61624	+.00410
30	-.61782	+.00158

Electrolytic Copper Strip

0	-.20694	--
5	-.19141	-.01553
10	-.18918	-.00223
15	-.18830	-.00088
20	-.18731	-.00099
30	-.18661	-.00070

RESULTS

Tables I to IX inclusive (attached as appendix) tabulated data of galvanic cells.

Graphs number I to IX inclusive - graphical representation of above data.

Table X - tabulated data of equilibrium potentials.

DISCUSSION OF RESULTS

1. Copper against 50-50 (Pb-Sn) solder (graph #1). The solder was anodic to the copper in both the plain Sea Water and acidified solution. An equilibrium value of .029 milli-amperes per square inch was reached in both electrolytes; in the case of the Sea Water an elapsed time of 24 hours was required while with the addition of HCl the value was reached in one hour. Attention is particularly called to the fact that the solder was anodic throughout; because it will be later shown that this is not the case in a soldered joint of these two materials. In other words this test is practically valueless in attempting to predict the action of a solder upon a metal because in the latter case we are interested only in the alloy formed. A blue precipitate was formed in the Sea Water which was dissolved upon the addition of HCl.

2. Copper against solder (Pb 78.8 - Cd 19.7 - Zn 1.5)(Graph #2).

There is nothing of particular interest displayed here. Once again the solder is anodic in both electrolytes; maintaining a higher value in the more acidic solution. The solution was clear throughout.

3. Copper against Copper + 50-50 solder (heat treated)(Graph #3).

This cell is of particular interest in that it shows the effect of alloy formation and the impossibility of correlating such action with the results obtained with the plain solder, (Graph #1). Here, in the weakly acidic Sea Water (P_H 6.25), the copper was cathodic for one hour and there was sharply attacked, gradually falling off to reach an equilibrium value in about 40 hours. However, in the acidified solution the copper was anodic at all times and its rate of corrosion as shown by the current density was much higher. This test implies that a soldered joint of this composition would be expected to fail much more rapidly with an increasing acidic content of the atmosphere. This test was performed to form a basis for a comparative study of the effects of a tinless solder under identical conditions. Inci-

dentally the results closely corroborated the work of Paul D. Merica upon tin coated copper roofing in similar solutions. A great deal of difficulty was experienced in removing the top layer of unchanged solder and probably small proportions of the eutectic (Cu-Sn). This must be done in order to determine the properties of the underlying alloy layers which are the true corrosive agents. The previous work of Dr. Merica was invaluable in solving this difficulty, because he experienced the same trouble. The presence of tin will always make the copper cathodic and thus obscure the true conditions. Boiling in hot HCl removed this outer layer and gave the values obtained. A photo-micrograph (page) clearly shows the alloy formation. The solutions became a deep blue.

4. Copper against Copper + Cadmium solder (heat treated)(Graph #4).

The action of this cell shows the markedly superior properties of this tinless solder over the 50-50 (Pb-Sn) solder. The heat treated specimen was anodic throughout the test in both electrolytes. In the case of the Sea Water it reached a value of zero in about 170 hours and remained there, which is a very desirable property. The results of this laboratory test indicate that the copper would be protected

at all times and a point would be reached at which theoretically galvanic corrosion would cease. Of course no such sublime properties are claimed, but its superiority over tin solder is conclusively proven. A photo-micrograph (page) shows the alloy formation. The solution turned a deep blue.

5. Iron against 50-50 (Pb-Sn) solder (Graph #5).

In this cell the iron was cathodic for one minute and anodic for the rest of the test in the Sea Water electrolyte. In the more acidic solution it was cathodic throughout. A heavy rust precipitate was formed in the Sea Water, which later upon the addition of HCl was partially dissolved, leaving the solution a light yellow.

6. Iron against Cadmium solder (Graph #6).

In this case the iron was protected throughout the test (cathodic) in both solutions, with a higher value in the more acidic electrolyte. The solution was clear at all times.

7. Iron against Iron + 50-50 (Pb-Sn) solder heat treated, (Graph #7).

In Sea Water the iron was anodic for the duration of the test, (200 hours). A heavy rust precipitate formed on the iron anode and settled on the bottom of the beaker. The addition of HCl to the

electrolyte caused the solution to clear up considerably to a light yellow, and the iron to become cathodic in about three hours. Attention is particularly called to the time element in this reversal of polarity (in the more acidic solution) and the value of about .14 milli-amperes per square inch density at the end of the run. It is evident once again by a comparison of this cell with that of the iron against the plain solder that the action of the solder alone is no criteria of the results to be expected from the alloy formed in the actual soldered joint. A photo-micrograph (page) shows the presence of alloy formation.

8. Iron against Iron + Cd. solder (heat treated)(Graph #8).

In Sea Water the iron was cathodic for 41 hours and then became anodic. This latter reversal was marked by the appearance of an appreciable rust precipitate. Thus although this solder does not protect the iron indefinitely, it is better than the tin solder which afforded no protection at all. In the acidified solution the iron was cathodic reaching a value of .026 milli-amperes per square inch in 200 hrs. At this point a comparison of results with those of the previous cell shows a much slower corrosive rate and equal protection afforded by this

Cadmium solder on iron. A weakly acidic solution seems to foster corrosion in both cases, but the Cadmium solder withstands this effect for some time. A photo-micrograph is included (page).

9. Iron against Terne plate + Cd. solder (heat treated)(Graph #9).

This cell is remarkably similar to that of iron against iron + 50-50 solder (heat treated) cell #8. It acts in the same way, the iron being anodic in the Sea Water and reversing itself, becoming cathodic with the addition of HCl. The presence of even a very small percentage of tin evidently has a very corrosive effect in a slightly acidic solution.

In the more acidic solutions it reverses itself after about 27 hours (considerably longer than in the case of aforementioned cell #8), and reaches an equilibrium value of about .055 milli-amperes. Thus, there seems to be little to be gained by the use of this tinless solder upon such a material, i.e., one containing a coating in which tin is present. There seems little doubt that the presence of very small proportions of tin materially accelerates corrosion in the case of iron.

10. Potential determinations.

Determination of the equilibrium potential referred to the hydrogen scale was conducted for copper iron, 50-50 (Pb-Sn) solder, and two tinless solders of composition, (Pb 78.8 - Cd 19.7 - Zn 1.5); (Pb 80.7 - Cd 17.3 - Bi 2). As previously discussed these values are not actually equilibrium values, because no such point was reached, but they are a true indication of the relative magnitude of the absolute potentials of these materials with electrolyte chosen. Inasmuch as the object of these determinations was to attempt to correlate and predict the corrosive effects of these solders, a relative value is sufficient. It is not intended to convey the impression that these figures are inaccurate but simply that they are only reliable to the extent of ± 0.005 volts. The potentials were continually falling and the value stated hereafter was taken when the fall was negligible in the time interval observed. A table of values obtained is included (page).

There is no indication that these values could be used in any way to predict corrosive effects. Once again it must be noted that in the corrosion of soldered joints it is the alloy layer formed which is of interest and not the unaffected solder.

However it is interesting to note that if the material tested be arranged in a series as follows with the basest materials at the top, it is possible to predict the corrosive effect in Sea Water or weakly acidic solutions:-

Corroded End	(Anodic) or base metals	Potential
Solder	Pb 80.7 - Cd 17.3 - Bi 2	-.46632
Solder	Pb 78.8 - Cd 19.7 - Zn 1.5	-.46400
	Iron	-.37182
Solder	Pb 50 - Sn 50	-.25100
	Copper	+.05939

Protected End (Cathodic) or noble metals

Connecting any two metals in the list with each other will cause the one higher on the list to corrode, (become anodic). Referring to the graphical representation of the four galvanic cells in which the solder was used as one pole, it is also evident that the further these two materials are apart on this list the greater the magnitude of the corrosive effect, (i.e. the current density). This relation immediately suggests the possibility that if the equilibrium potential of the alloy or alloys formed in a soldered joint could be determined, some very

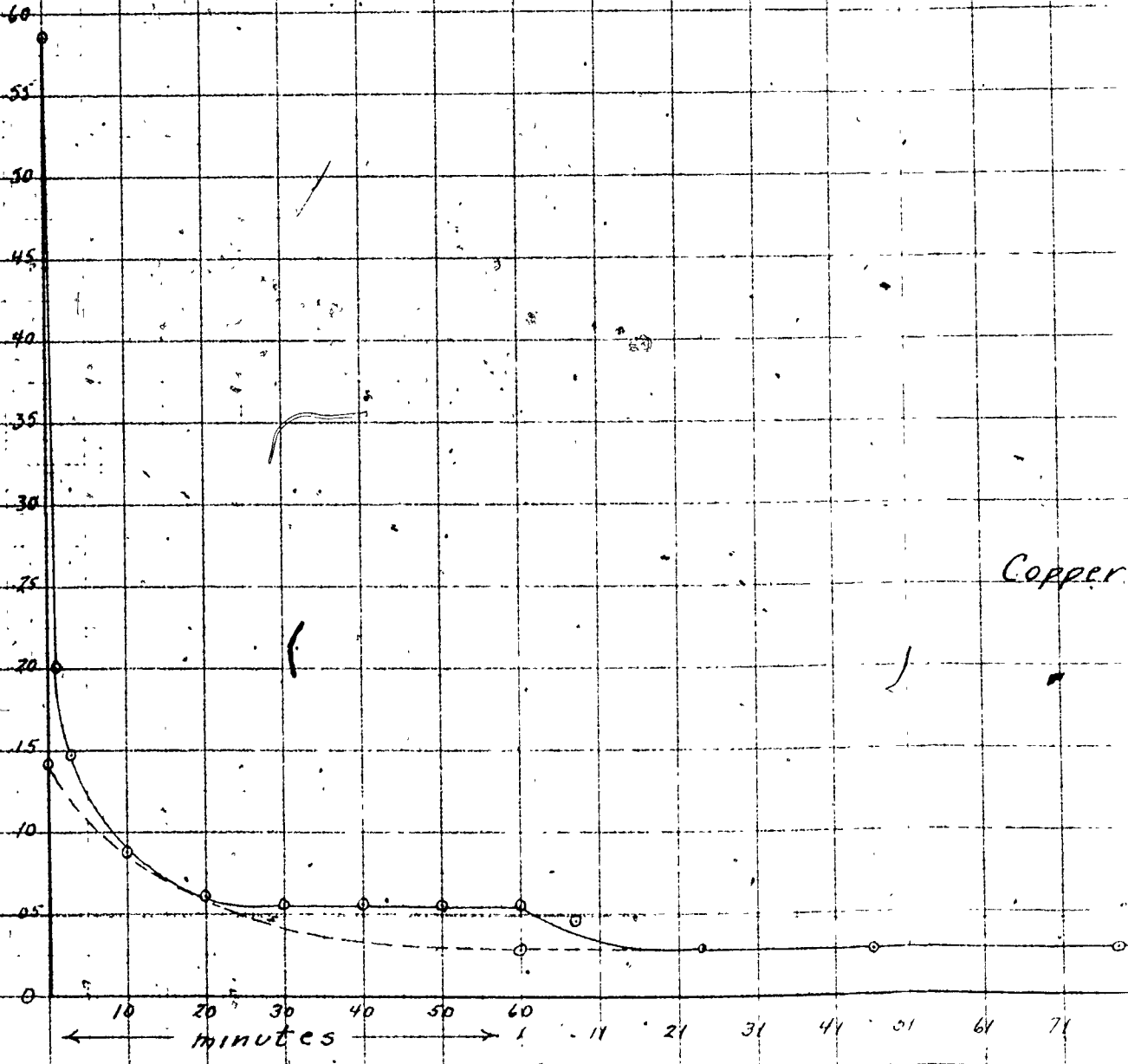
valuable information might be obtained. This field offers some very interesting possibilities for further research.

Before leaving this discussion it might be well to explain the method of arriving at the equilibrium potential values given previously, because they are not the same as the observed values given in the table following. This is because the value desired is the potential referred to the hydrogen scale, and the readings obtained were those referred to the saturated calomel half cell. Inasmuch as the potential of this cell is $+0.246$ volts and all readings were minus the true equilibrium value of the specimens examined (referred to hydrogen) is the vector sum of these two quantities. This can be best illustrated by taking copper as an example.

$$\begin{array}{ccc}
 \text{H/H}^+ // \text{Hg}^+ / \text{Hg} & & \text{Hg/ Hg}^+ // \text{Sea Water/Cu} \\
 \xrightarrow{\quad} & & \xleftarrow{\quad} \\
 +.246 & & -.18661 \\
 \text{resultant} \xrightarrow{\quad} & & \\
 +.05939 & &
 \end{array}$$

Current Density - Milli-amperes

Copper



Copper against 50-50 Pb-Sn solder

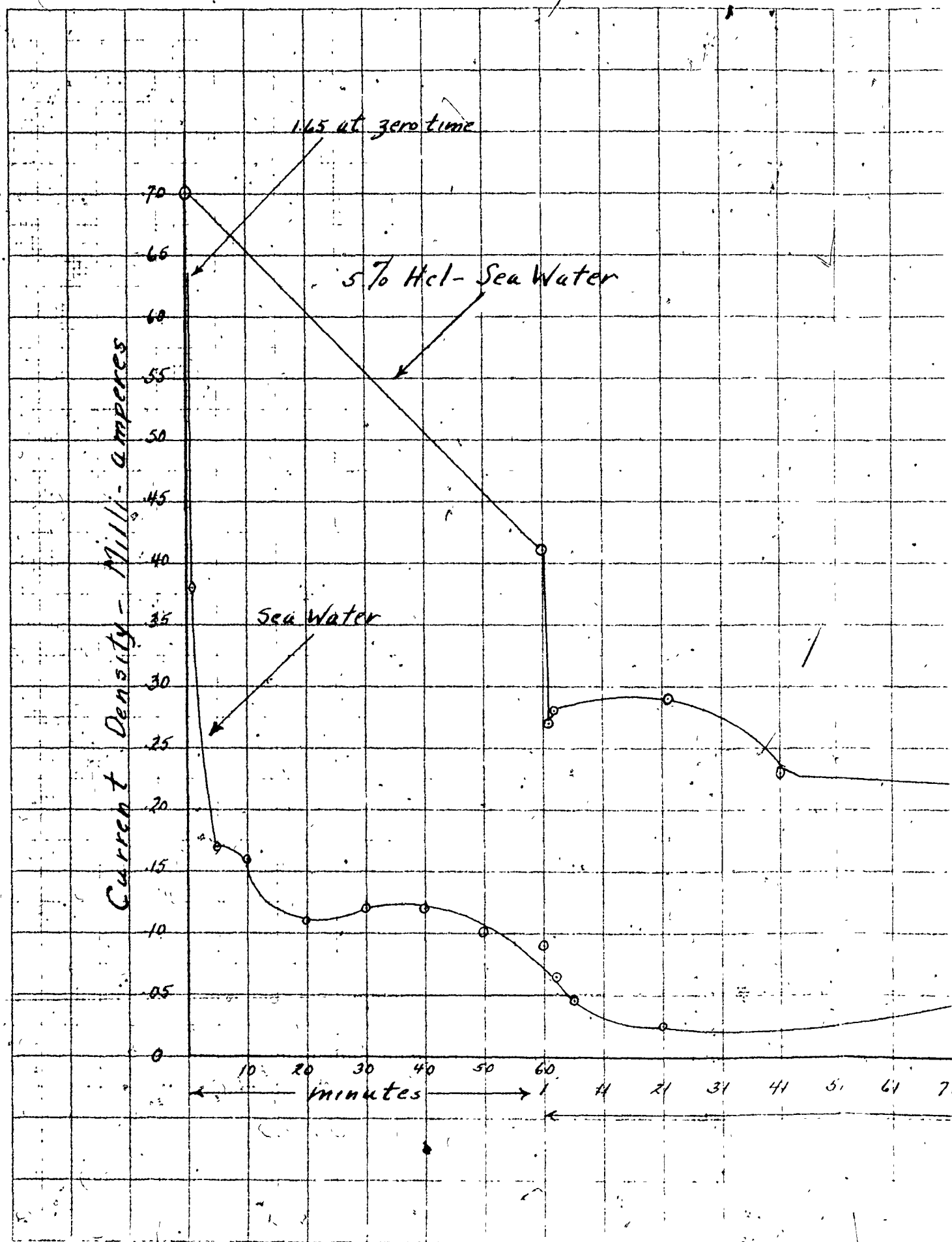
Anode — Solder

Electrolytes

synthetic Sea Water

----- " " " — 5% HCl

41 51 61 71 81 91 101 111 121 131 141 151 161 171 181 191 201
hours

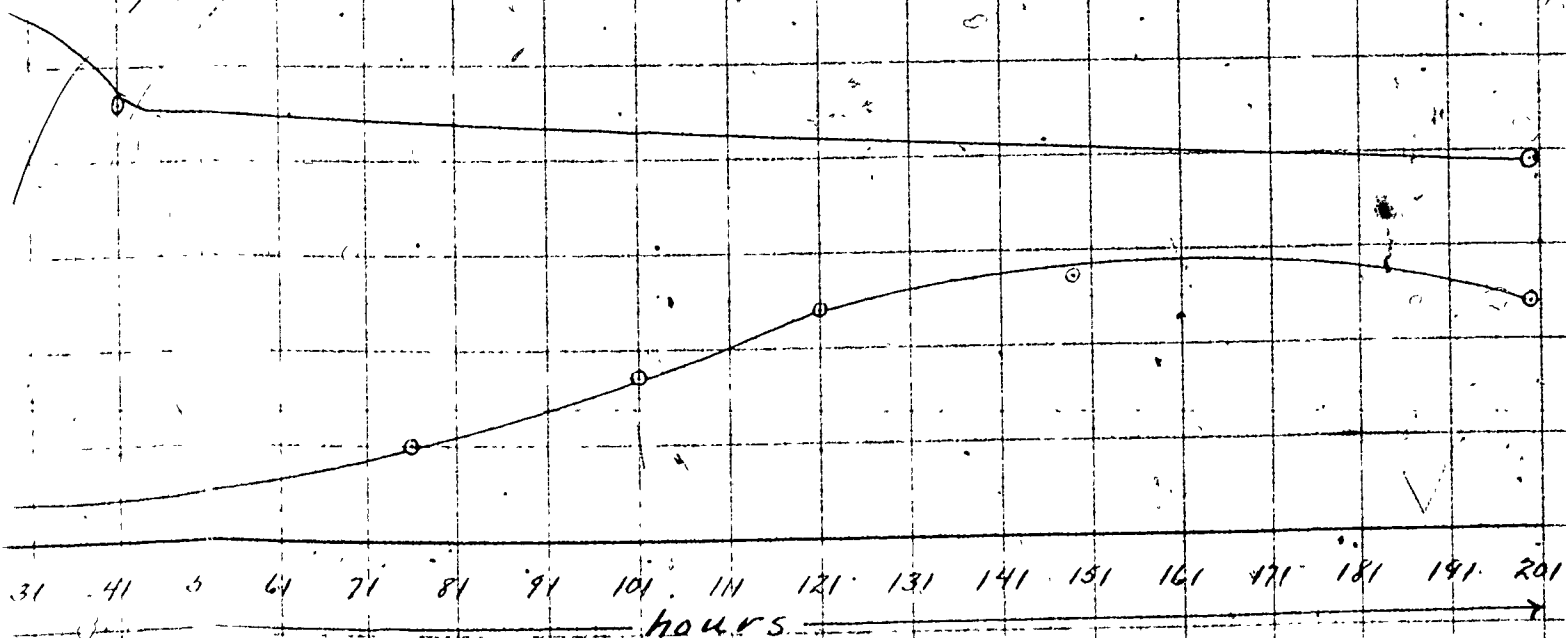


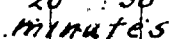
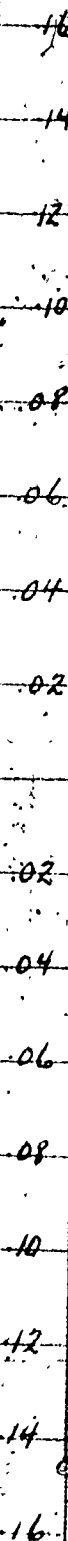
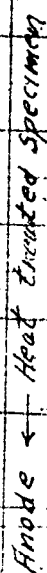
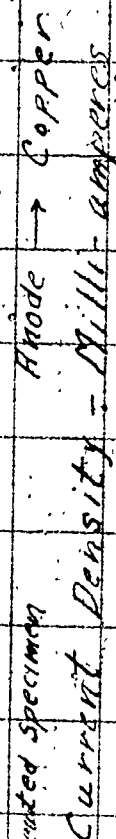
Copper against solder.

Pb	78.8%
Cd	19.7%
In	1.5%

Anode - solder

Electrolytes as indicated





Electro
Copper
and

Electrodes:

Electrolytic Copper strip

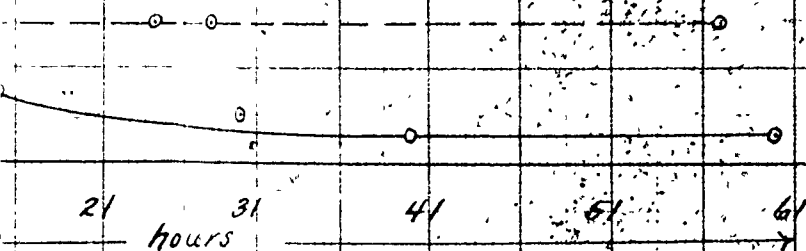
vs.

Copper strip dipped in 50-50 solder (Pb-Sn)
and heat treated at 500°C for 5 hrs.

Electrolytes:

Sea Water

Sea Water - 5% HCl



Current Density - Milli-amperes

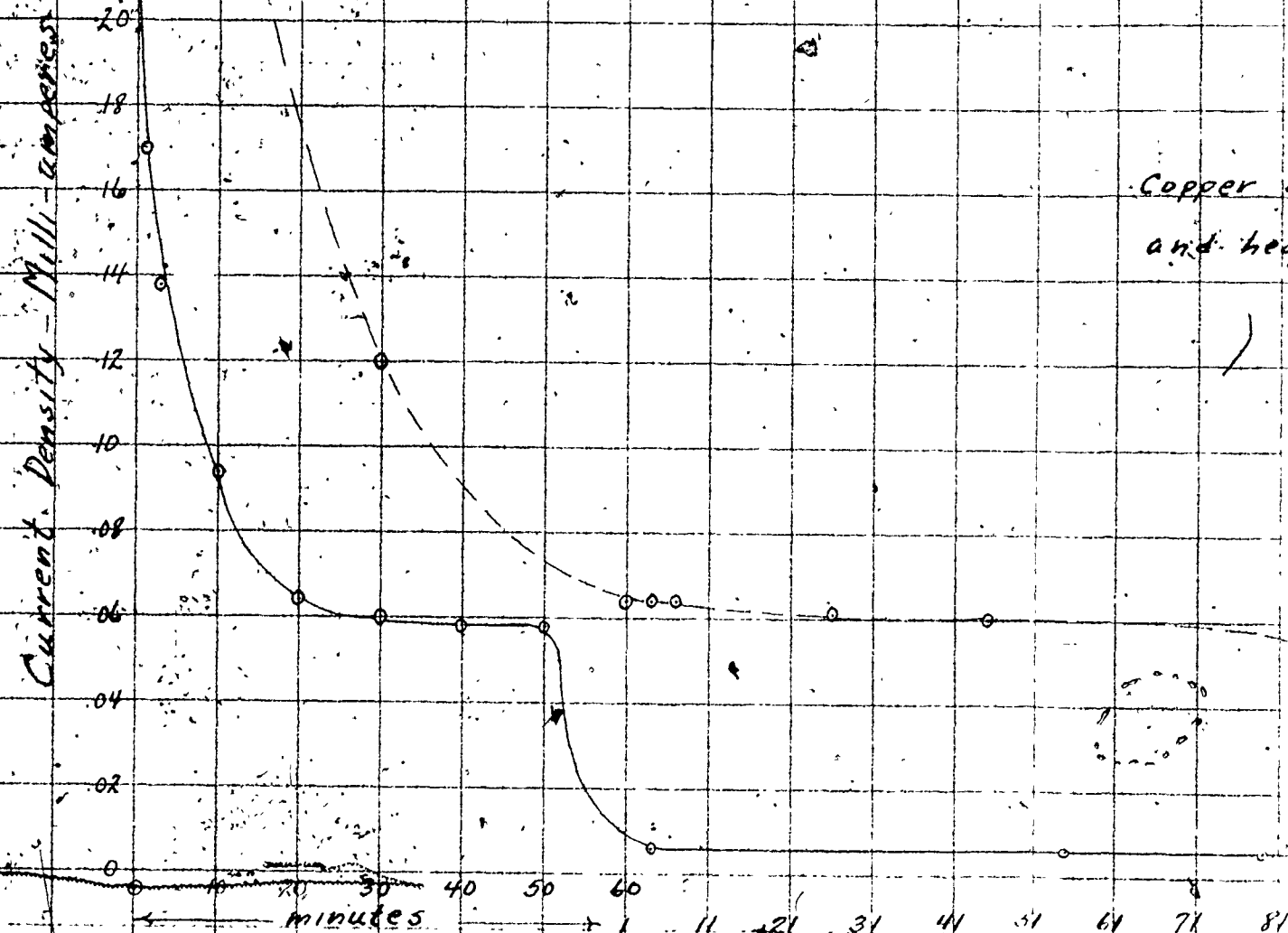
20
18
16
14
12
10
08
06
04
02
0

minutes

Instantaneous value .44
Instantaneous value .38

Copper d.
and heat

10 20 30 40 50 60 70 80
1 11 21 31 41 51 61 71 81



Copper

vs.

Copper dipped in solder { Pb. 78.8
Sn. 19.7
Zn. 1.5

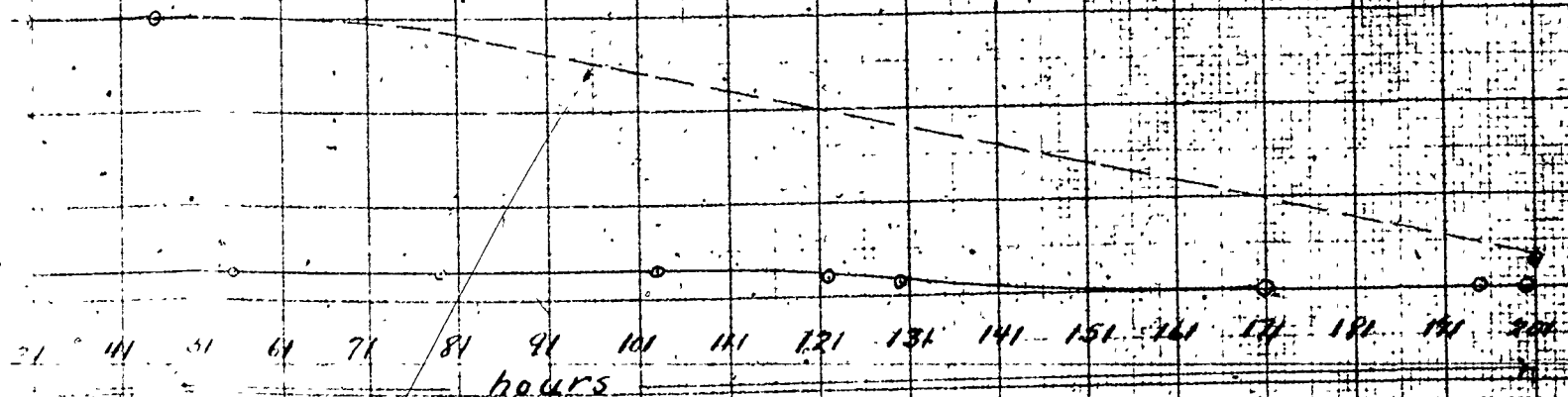
and heat treated at 500°C for 5 hrs.

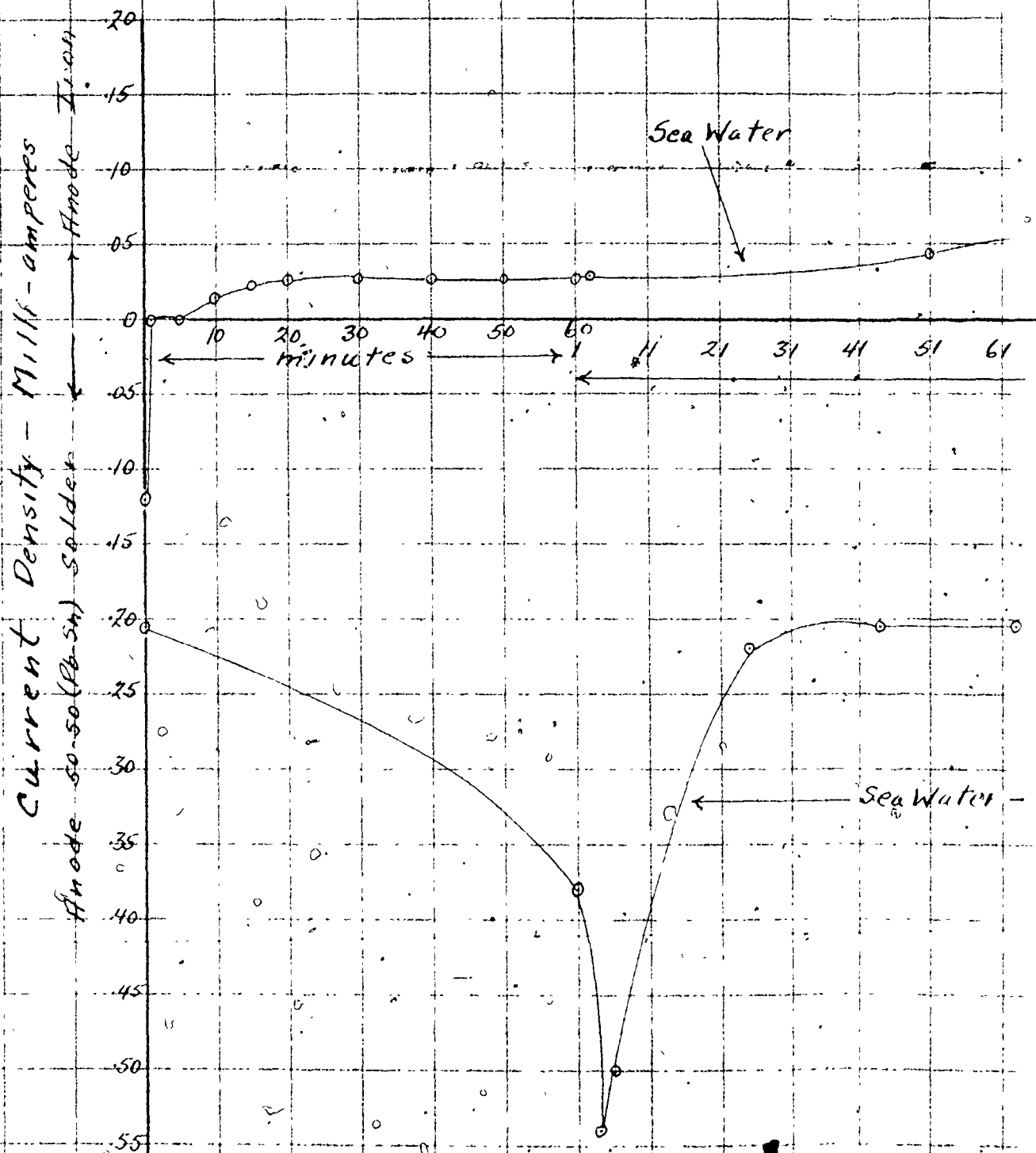
Electrolytes:

— Sea Water

- - - Sea Water - 5% HCl

Anode → heat treated specimen





Iron

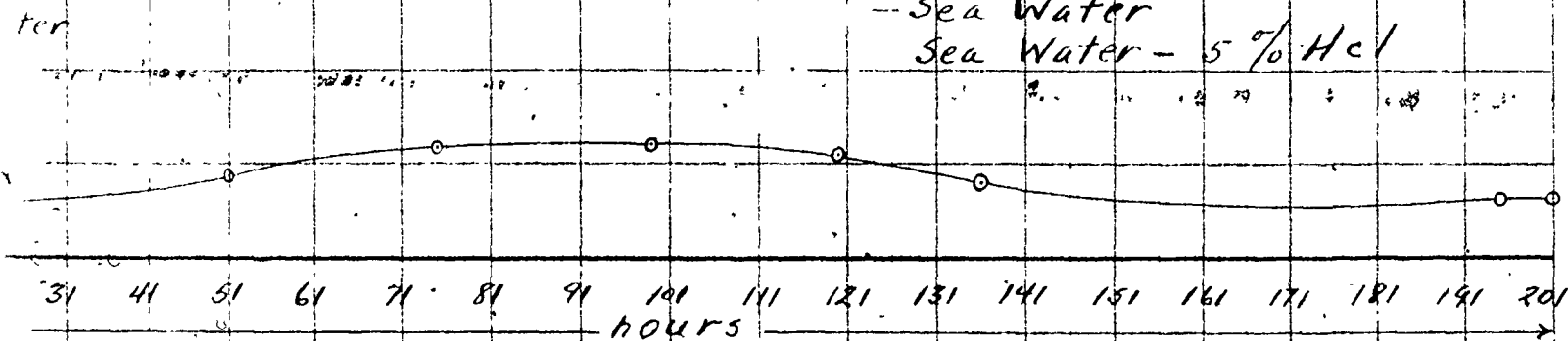
vs.

50-50 (Pb-Sn) solder

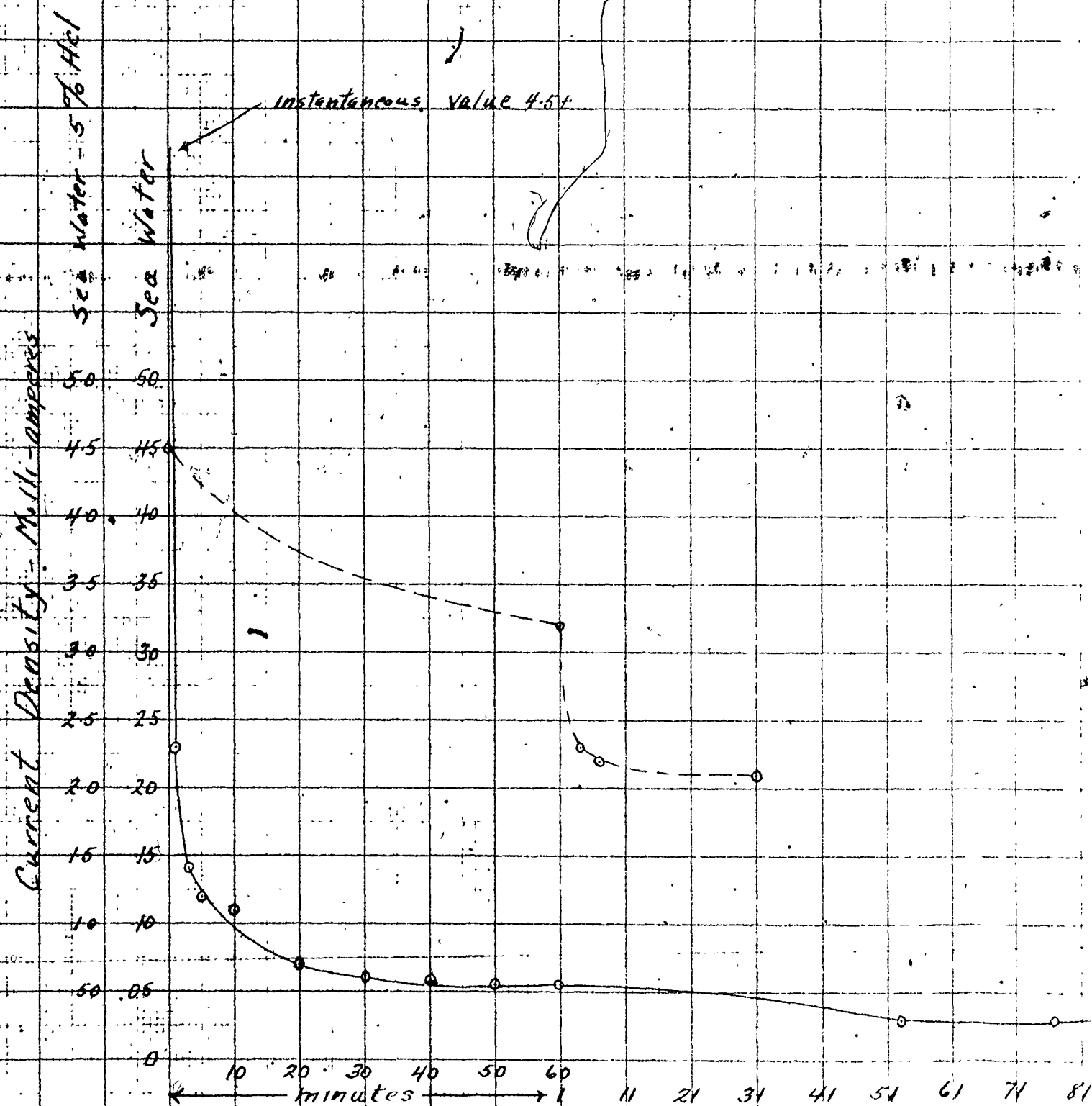
Electrolytes:

— Sea Water

Sea Water - 5% HCl



Sea Water - 5% HCl

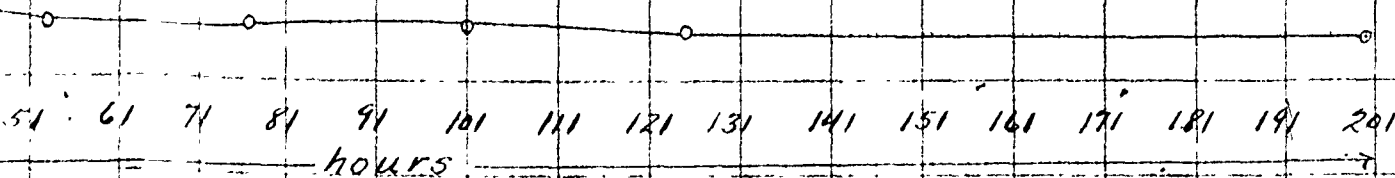


Iron
VS
Solder { Pb 78.8
Cd 19.7
Zn 1.5

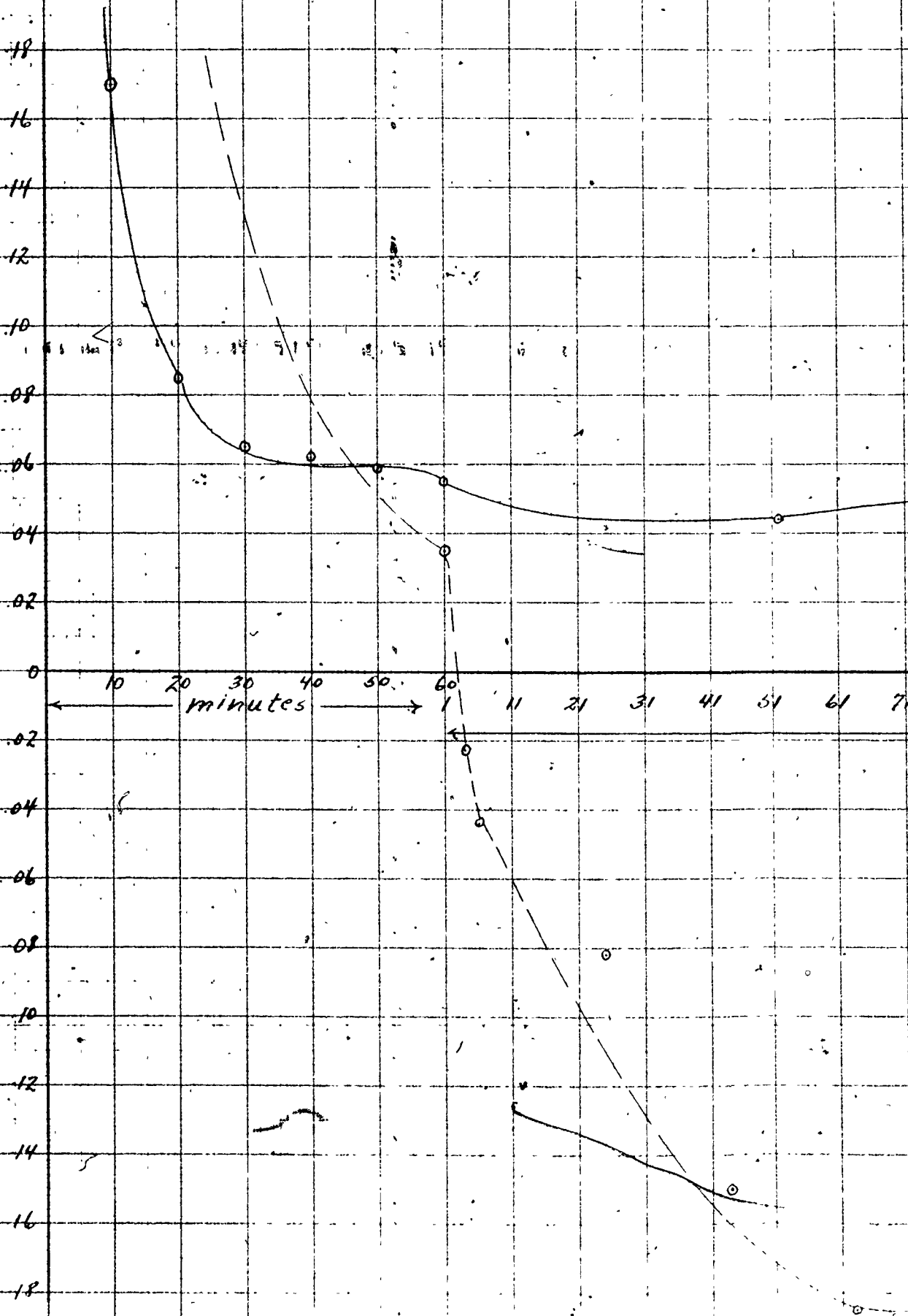
Anode - Solder

Sea Water

Sea Water - 5% HCl



Current Density - Milli amperes
Anode - Iron
Anode heat treated specimen



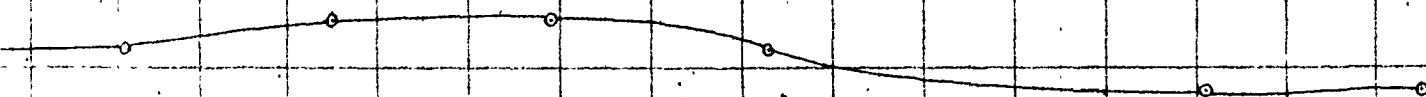
Iron
vs.

Iron strip dipped in 50-50 (Pb-Sn) solder
heat treated to 500°C for 5 hours

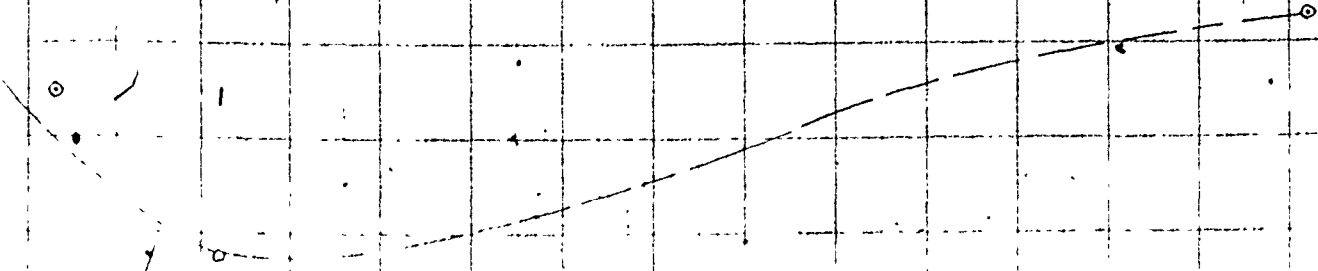
Electrolytes:

— Sea Water

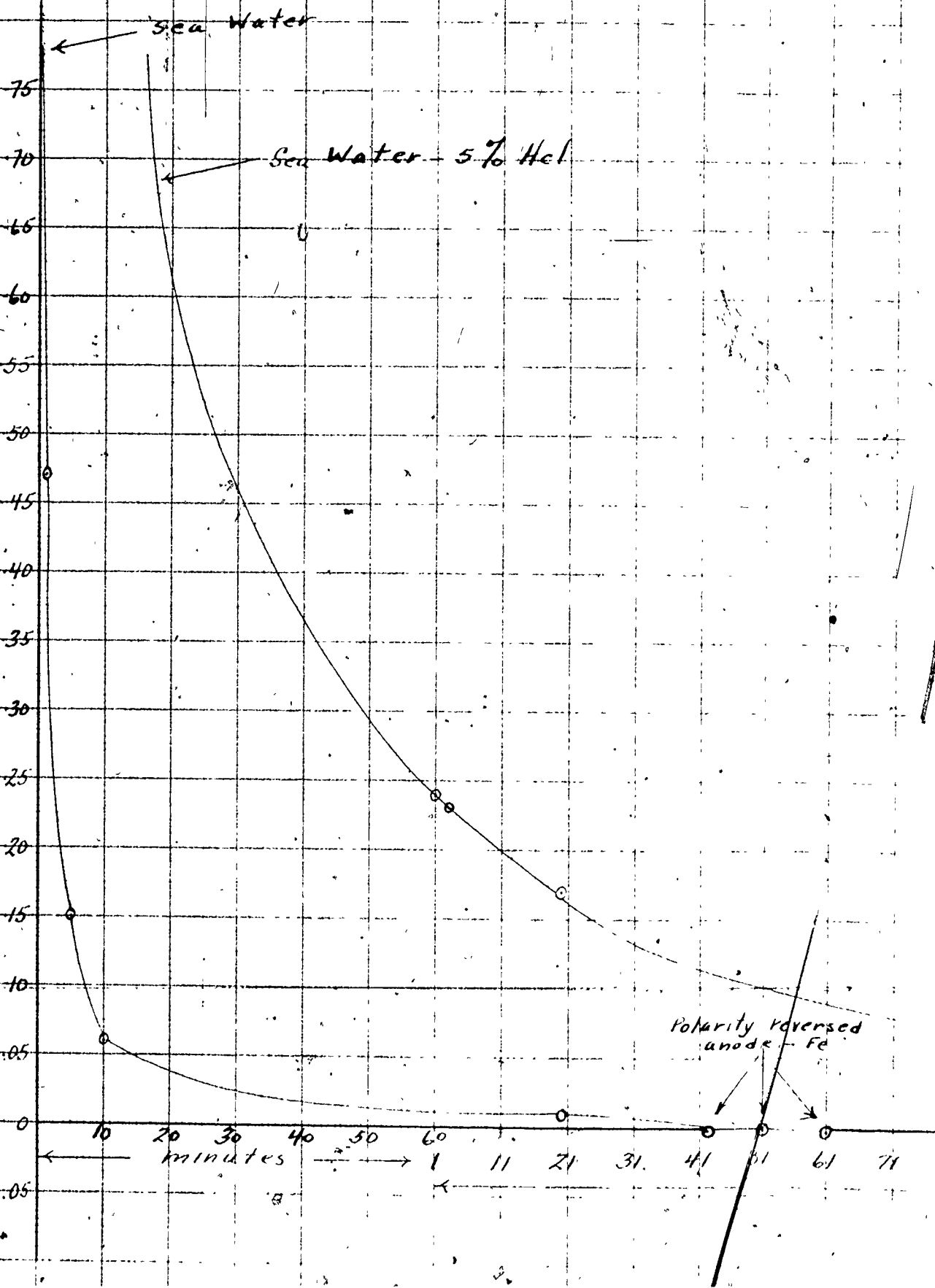
- - - Sea Water + 5% HCl



4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
HOURS



Current Density Milli-amperes
Anode - heat treated specimen



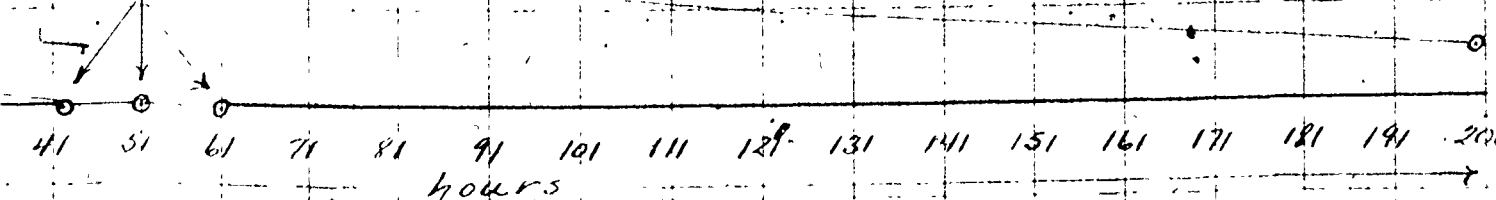
Iron

vs.

Iron strip dipped in solder of
composition Pb 78.8 - Cd 19.7 - Zn 1.5
heat treated at 550°C for 5 hrs.

Heat treated specimen anodic
except after 41 hrs in sea water
where Iron is anode with value
of .003 milli-amperes.

Polarity reversed
anode - Fe



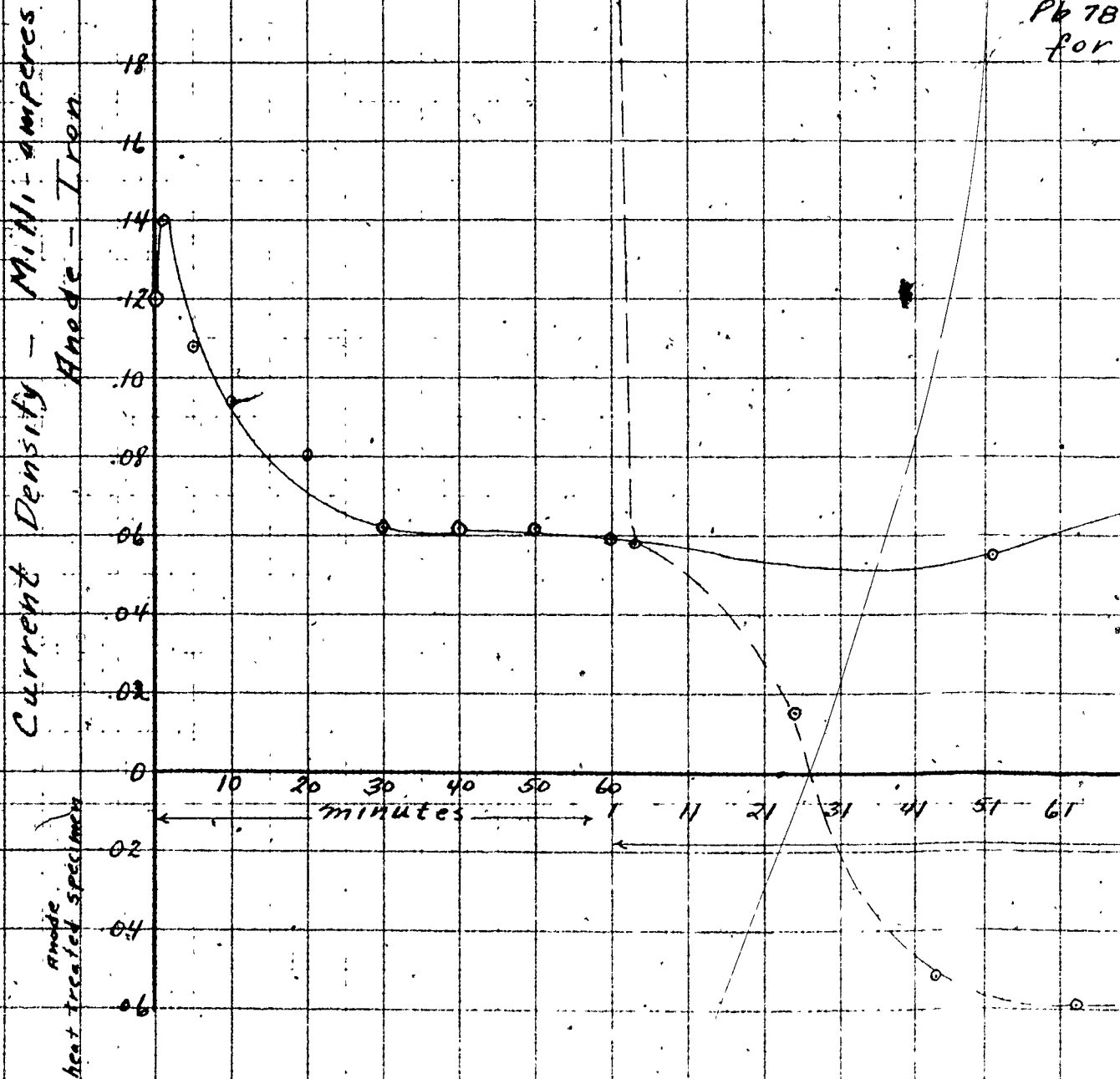
Current Density - Milli-amperes
Anode - Iron

Anode
heat treated specimen

28
26
24
22
20
18
16
14
12
10
08
06
04
02
0
02
04
06

10 20 30 40 50 60 11 21 31 41 51 61
minutes

Terne
Pb 78
for



Iron

vs.

Terne plate

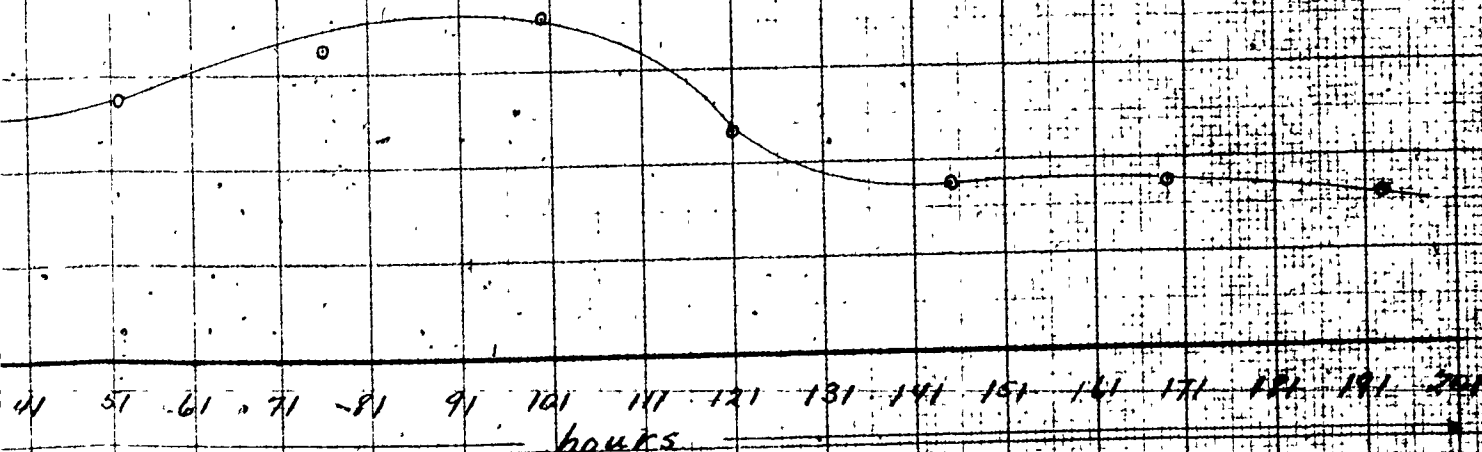
dipped in solder of composition

Pb 78.8 - Cd 19.7 - Zn 1.5 heat treated at 500°C
for 5 hrs.

Electrolytes:

Sea water

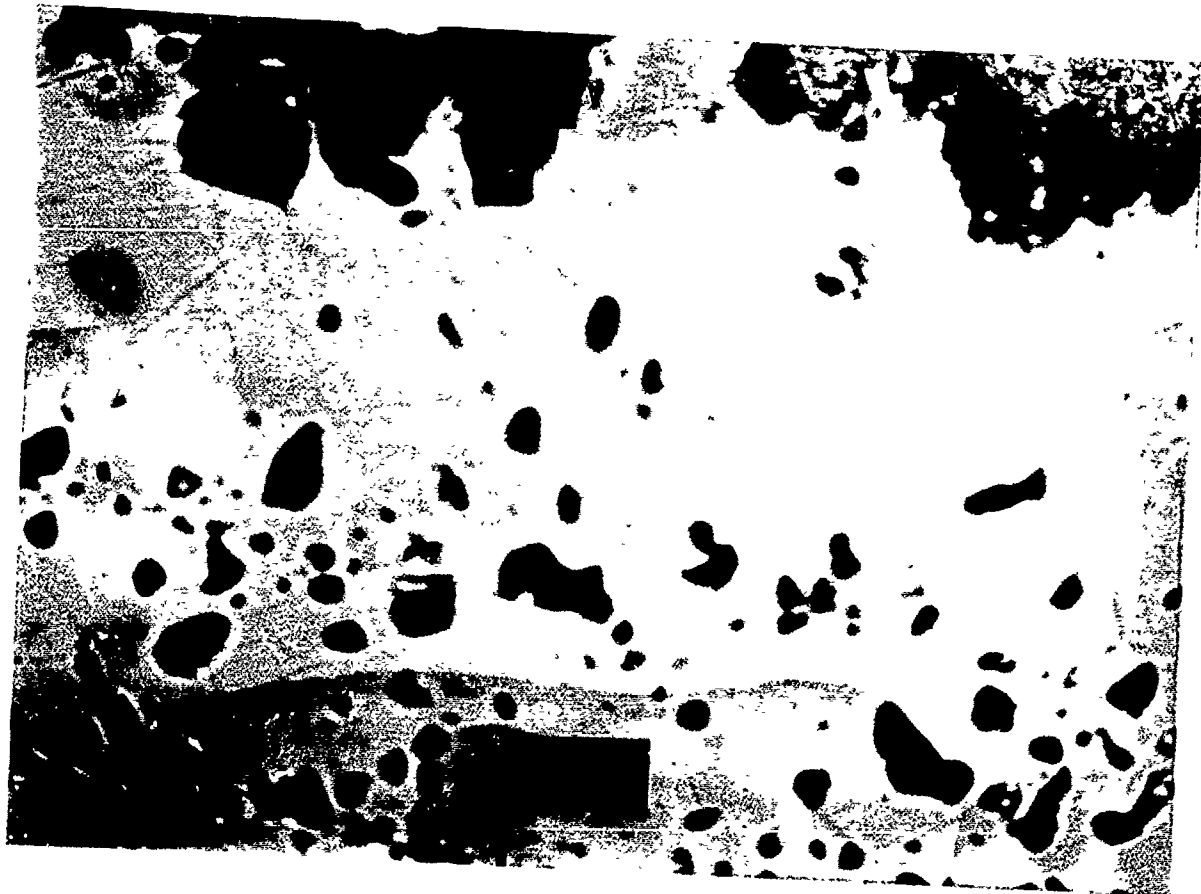
Sea water - 5% HCl



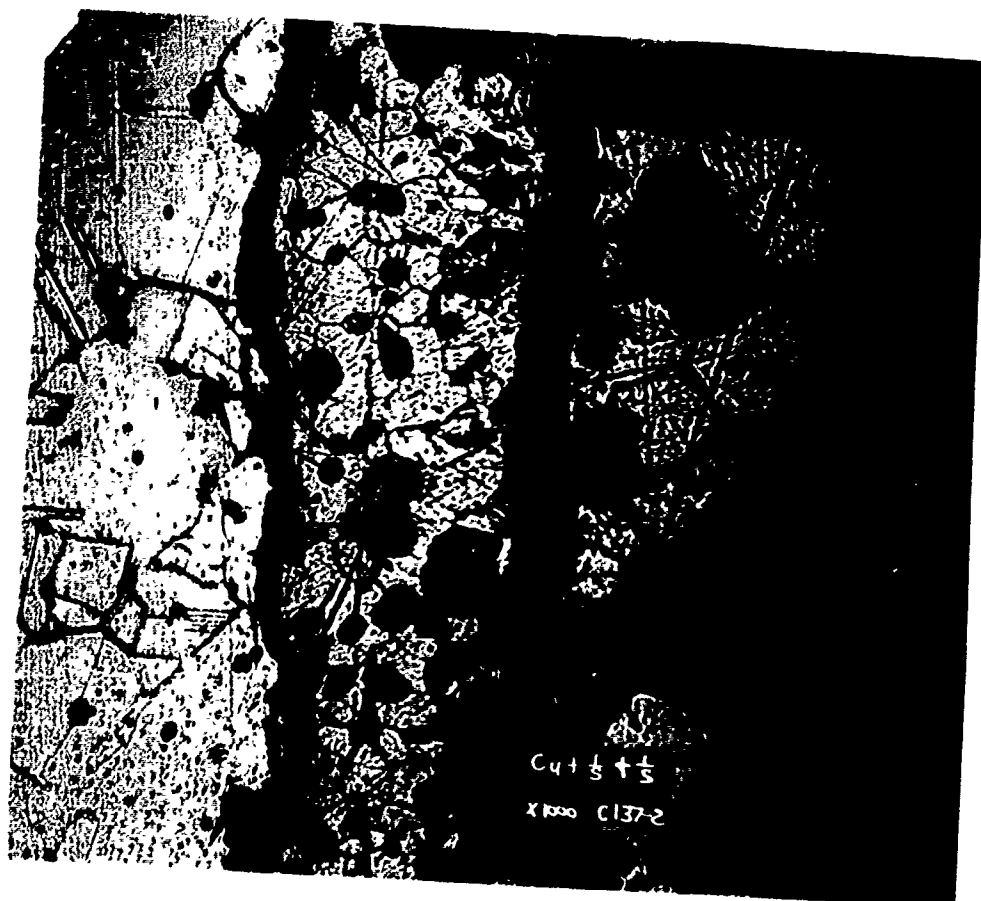
Cu + 50-50 (Pb-Sn) solder (heat treated)

Magnification:	300X
Etching Reagent:	Unetched
Remarks:	Evidence of two alloys as shown by bright areas around unaffected solder (black) and light gray. Copper visible in lower left hand corner.

Magnification:	1000X
Etching Reagent:	(FeCl ₃ - HCl - CH ₃ OH)
Remarks:	Copper at bottom. Alloy layers plainly visible. Block is solder which has been overetched and dis- solved.



C 137-1



C4 + 1/2 + 1/2

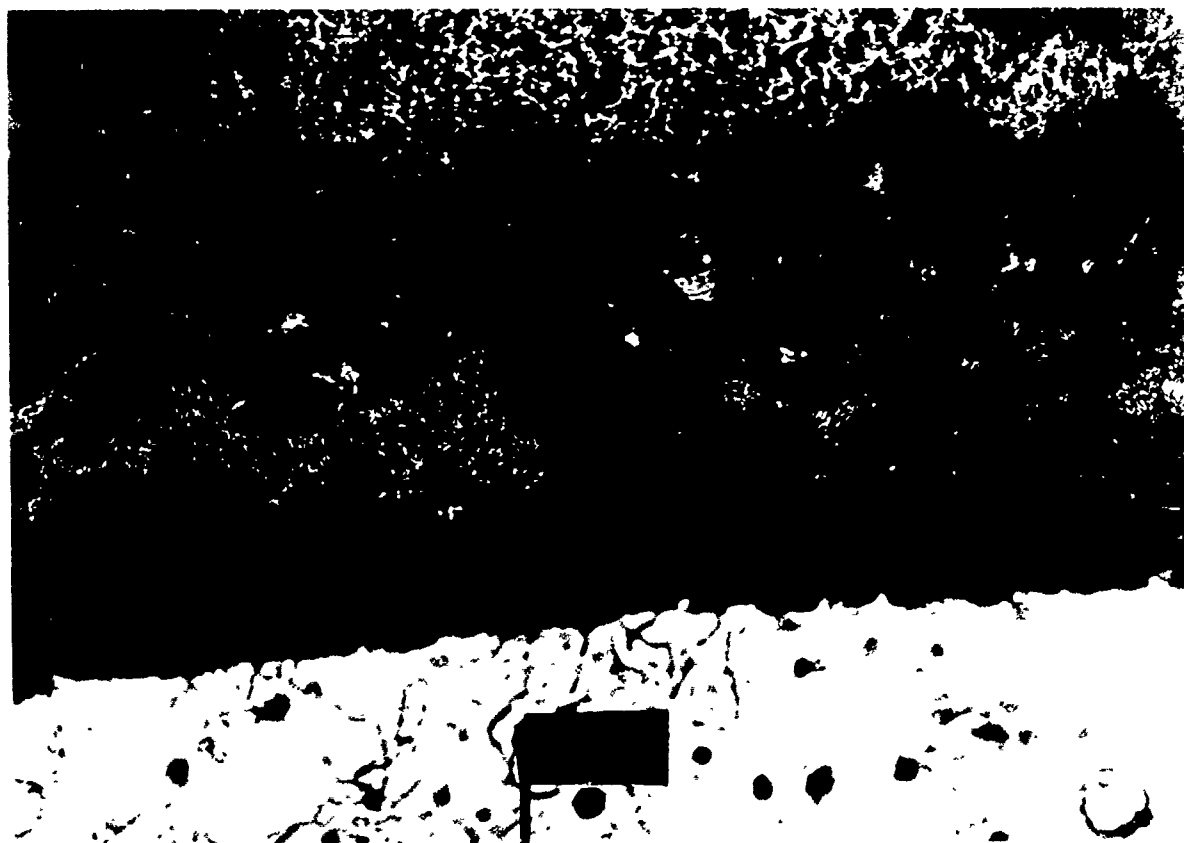
X1000 C137-2

Cu + Solder (Pb 78.8 - Cd 19.7 - Zn 1.5) heat treated

Magnification: 500X

Etching Reagent: (FeCl₃ - HCl - CH₃OH)

Remarks: Copper at bottom, unaffected solder at top, alloy layer between.



C 137-3

Steel # 50-50 (Pb-Sn) solder, heat treated

Magnification:	1000X
Etching Reagent:	2% Nital
Remarks:	Steel at top of picture. Note evidence of at least two alloy layers.



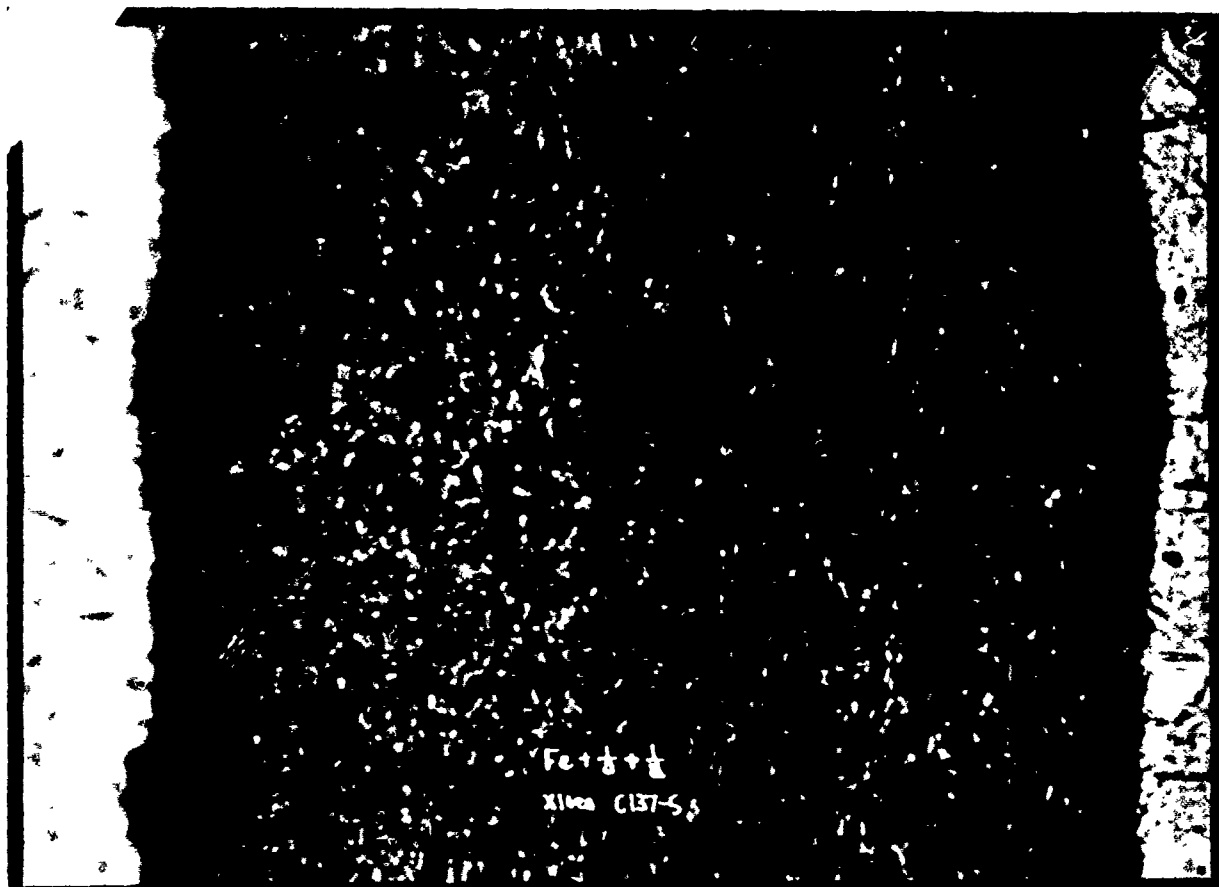
C137-4

Steel + Solder (Pb 78.8 - Cd 19.7 - Zn 1.5) heat
treated.

Magnification: 1000X

Etching Reagent: 2% Nital

Remarks: Structure of solder
clearly defined, but
very little evidence
of alloy formation.
Steel on the left -
solder - copper
electroplate.



CONCLUSIONS

1. Arrangement of the materials tested in an electromotive series determined by their equilibrium potentials, will afford a means of predicting the direction of flow of current, (of more interest, the anode), where any two are electrically connected in a neutral or weakly acidic solution.
2. Copper is cathodic to 50-50 (Pb-Sn) solder in Sea Water and Sea Water - 5% HCl solutions.
3. Copper is in general anodic to the alloy formed on soldering with 50-50 (Pb-Sn) solder in both above mentioned solutions.
4. Copper is cathodic to (Pb 78.8 - Cd 19.7 - Zn 1.5) solder in both solutions.
5. Copper is cathodic to the alloy formed on soldering with this tinless solder in both solutions.
6. The presence of tin in a solder for use on copper has a very corrosive effect which is accelerated by the greater the acidity of the electrolyte.
7. A solder of composition (Pb 78.8 - Cd 19.7 - Zn 1.5) protects the copper in both weakly and strongly acidic solutions. In the former case it seems especially valuable in that here the flow of current approaches zero.
8. Iron is anodic to 50-50 (Pb-Sn) solder in Sea Water and cathodic in Sea Water - 5% HCl.

Conclusions (cont'd)

9. Iron is cathodic to (Pb 78.8 - Cd 19.7 - Zn 1.5) solder in both solutions.
10. Iron is anodic to the alloy formed on soldering with 50-50 (Pb-Sn) solder in Sea Water electrolyte, and cathodic (after 3 hrs.) in Sea Water - 5% HCl solution.
11. Iron is cathodic for 41 hrs. to the alloy formed on soldering with the tinless solder in a solution of Sea Water, and then becomes anodic. In Sea Water - 5% HCl iron is cathodic throughout.
12. The presence of tin in a solder for use on iron has a very corrosive effect in a weak acid solution. In a strongly acidic solution the iron is protected after 3 hours but the current density becomes very high causing rapid corrosion of the anode.
13. A solder of composition (Pb 78.8 - Cd 19.7 - Zn 1.5) is far superior to the standard 50-50 tin solder for use on iron protecting the iron for 41 hours in a Sea Water solution (weakly acidic, Ph 6.25) and then becoming only slightly corrosive; while in a strongly acidic solution the iron is protected throughout, reaching a much smaller current density than is shown with the tin solder.

Conclusions (cont'd)

14. The presence of tin in the coating of the Terne plate destroys the value claimed for the use of the above Cadmium solder on iron. Even tin in such a small proportion has very harmful effects.
15. No definite correlation between the equilibrium potential of these solders and their corrosive effects can be determined. This is because in a soldered joint our corrosive influence is the alloy formed and not the solder.

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